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STUDIES OF THE FLUIDIZED LIME-BED COAL COMBUSTION DESULFURIZATION SYSTEM

Part 1 - Design of the High Pressure Fluidized Bed Combustion Lime Regeneration Pilot Unit - The FBCR Miniplant

Part 2 - Factors Affecting NO_x Formation and Control in Fluidized Bed Combustion

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16. Abstracts

The preliminary design of 650 KW pressurized (10 atmosphere) fluid bed coal combustor is described. The system will consist of a 12-inch ID combustor and a 5-inch ID regenerator, with provisions for continuous solids circulation between the two reactors. The results of an experimental study conducted with the objective of determining methods of simultaneously obtaining low SO_x and NO_x emissions from a fluidized bed coal combustor are reported. In fixed bed reactor studies, a reaction system involving NO, SO_2 and CaO was identified. The apparent order of this reaction was about 0.5 and it had a negative temperature dependence. The reduction of NO by CO over $CaSO_4$ also studied in fixed bed experiments and found to proceed at appreciable rates in the 1300 F to 1700 F, with an apparent activation energy of 6 to 8 kcal/gmole.

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FOREWORD

This report was prepared by the Esso Research and Engineering Company, Linden, N.J. for the Control Systems Division, Office of Air Programs of the U.S. Environmental Protection Agency (EPA) under Contract CPA 70-19. The work described in this report was performed over the period January 1, 1971 to December 31, 1971. Mr. S. L. Rakes was the Project Officer for EPA.

The authors wish to express their appreciation to Messrs. H. R. Silakowski and W. H. Reilly for performing the laboratory work described in this report, and to Mr. R. K. Bryant for preparing the detailed engineering drawings of the fluidized bed pilot unit designed as part of this program.

SUMMARY

Esso Research and Engineering Company has carried out a two phase program for the Office of Air Programs of the U.S. Environmental Protection Agency aimed at furthering the development of fluidized bed combustion of coal as a new, low-polluting boiler technique for use in electric power plants. In fluidized bed combustion, the coal is burned in a bed of solids kept fluidized by the combustion air and the resulting flue gas. Combustion temperature is typically controlled in the range of 1500 to 1700°F by locating steam raising surface in the bed and taking advantage of the excellent heat transfer characteristics and high heat capacity of the fluidized solids. Greater than 90% reduction in SO_2 emissions can be achieved by using calcined limestone as the bed material. At fluidized bed combustion temperatures, the lime reacts with the SO_2 and O_2 in the flue gas to form $CaSO_4$. By contacting the sulfated lime with a reducing gas at about 2000°F in a separate fluidized bed, the lime can be regenerated for reuse in the combustor. This reductive regeneration also produces a rich SO_2 by-product stream which can be used to produce sulfuric acid or elemental sulfur.

The first phase of the program carried out by Esso Research under Contract CPA 70-19 involved the development of a detailed design for a continuous fluidized bed combustion - lime regeneration pilot unit - the FBCR Miniplant. This unit was designed for operation at up to 10 atmospheres pressure based on studies by Westinghouse Research Laboratories showing a much greater incentive for a pressurized fluidized bed combustor used in conjunction with a combined gas-steam power generating cycle, than for an atmospheric system.

The FBCR-Miniplant design incorporates a refractory lined combustor and regenerator with continuous transfer of sulfated and regenerated lime between these reactors. The design parameters are:

	Combustor	Regenerator
Unit Dimensions		
• Diameter, internal (in)	12.5	5
• Height (ft)	28	19
Maximum Operating Conditions		
• Temperature (°F)	1,700	2,000
• Pressure (atm)	10	10
• Superficial Bed Velocity (ft/sec)	10	5
• Heat Released by Combustion (BTU/hr)	6,300,000	--
• Cooling Load (BTU/hr)	3,600,000	--
Maximum Material Rates		
• Air (SCFM)	1,200	90
• Coal (#/hr)	480	--
• Limestone (#/hr)	68	--
• Natural Gas (SCFM)	--	10
• SO_2 Output (#/hr)	--	40

Figures 1 and 2 show respectively the overall system flow plan and assembly drawing for the FBCR Miniplant. The design calls for the combustor to be constructed from 24 inch pipe refractory lined to 12.5 inches internal diameter. It is designed with 5 flanged sections (each 3 feet long), a bottom plenum for air intake below the removable distributor plate, and an upper bed expansion section containing the gas discharge outlet to the cyclones. Combustor support would be provided by four legs attached to the first section above the grid. The reactors would be guided at 8 foot vertical intervals to accommodate thermal expansion. The regenerator design features an 18 inch shell refactory lined to 5 inches internal diameter.

Main fluidizing air for the combustor and regenerator would be supplied by a stationary compressor with a capacity of 1300 SCFM. The superficial bed velocity in the combustor and regenerator would be controlled automatically by differential pressure transmitters and control valves. In the combustor, the air would pass through the distributing grid, up through the fluidized

FIGURE 1

FBCR MINIPLANT FLOW PLAN

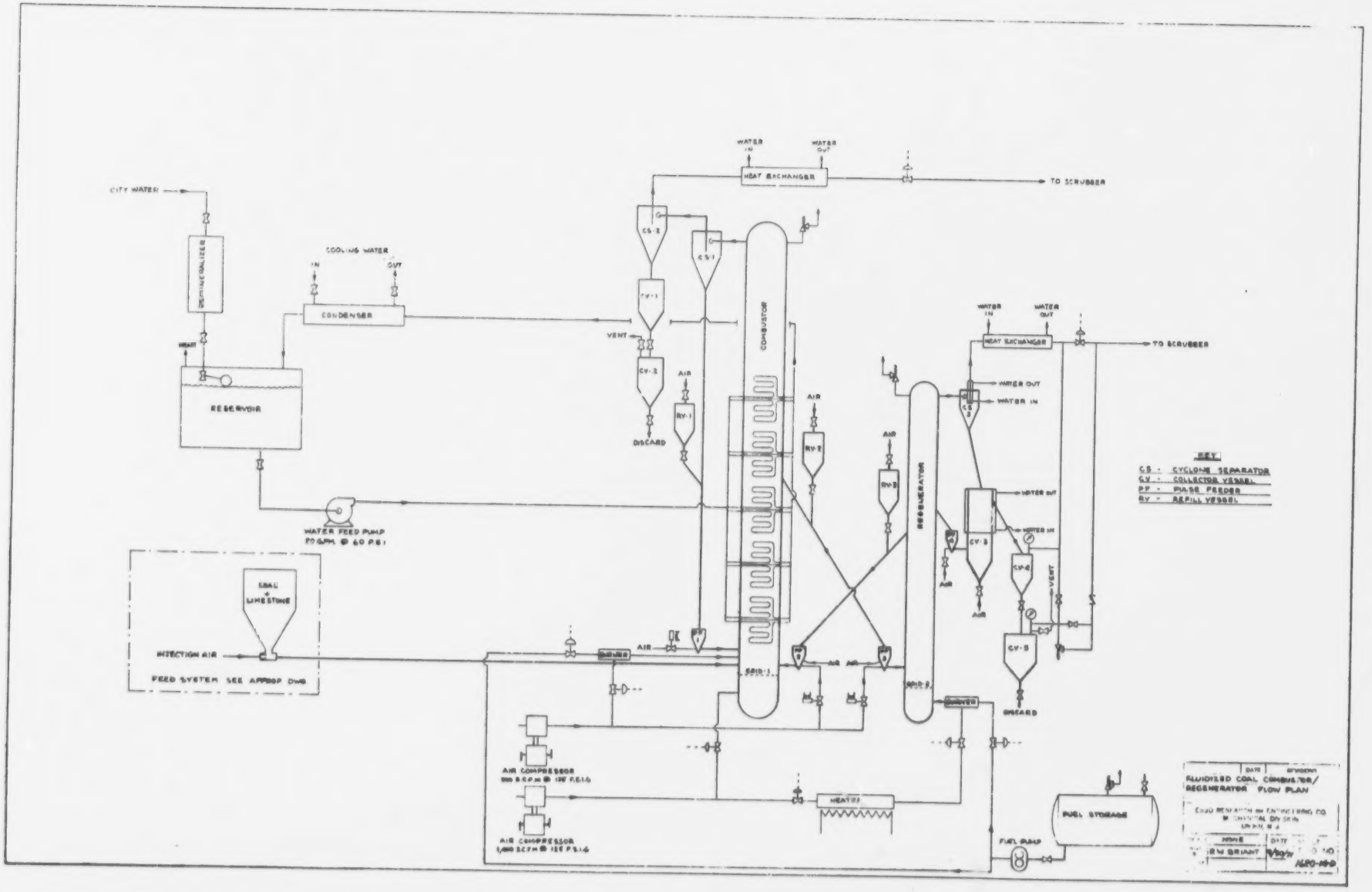
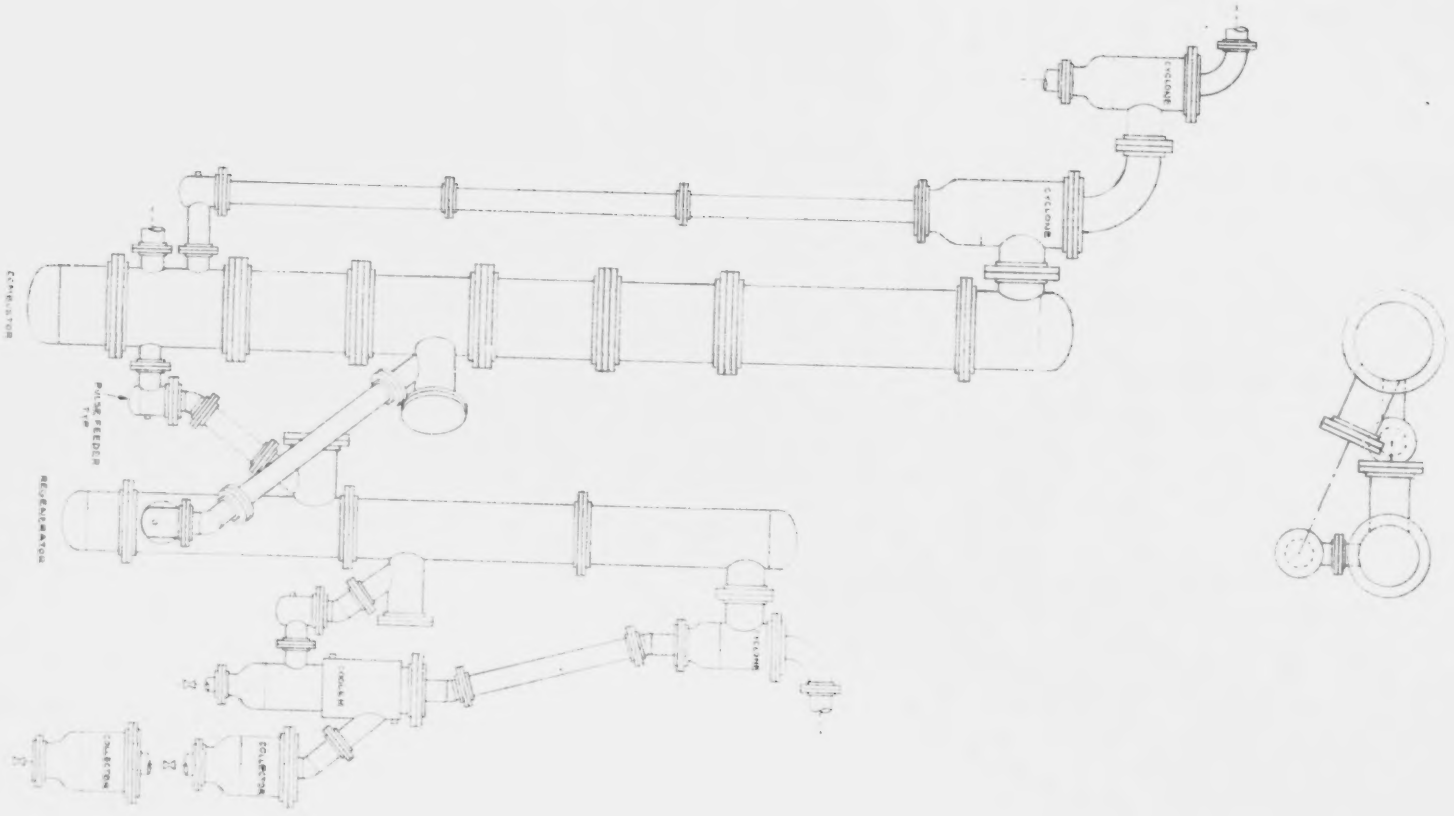


FIGURE 2

FBCR MINIPLANT ASSEMBLY



bed of solids, and out through two refractory lined cyclones for solids removal before being cooled in a heat exchanger. The pressure in the combustor would be maintained at a desired set point by a butterfly valve in the exhaust line positioned by a pressure transmitter and controller. Air for the regenerator could be electrically preheated for temperature control before passing into the reducing gas generator located at the bottom of the reactor. The reducing gas would pass through a ceramic distributor plate supporting the regenerating bed and then exit through a refractory lined cyclone and a heat exchanger before discharging through a butterfly valve. Pressure on the regenerator and combustor would be kept the same by a differential pressure control system and controller serving to position the butterfly valve in the regenerator discharge line.

Heat extraction and temperature control in the fluidized bed combustor would be accomplished by boiling demineralized water in 10 independent loops located in discrete vertical zones of the reactor. The water flows to these loops would be controlled by valves whose positions would be automatically changed to maintain bed temperature in each of the zones. The steam generated in these loops would be condensed and returned to a reservoir.

Coal and makeup limestone to the combustor would be fed continuously from a system designed for controlled solids feeding under pressure. Solids transfer between reactors, and discharge of solids from the system (i.e., from the regenerator reactor) would be accomplished using a pulsed air transport technique controlled by pressure differentials across and between these fluidized beds. This method of solids transfer has been studied in a plexiglas Cold Model Test Unit, the CMTU, built for this program. This unit consists of two 5.5 inch ID transparent vessels connected by two 1 inch ID transparent hoses for solids transfer. The CMTU was designed to operate at ambient temperatures and pressures up to 60 psig. In the CMTU, a

control panel permitted varying the gas velocities and pressures in the two vessels, the pulse air rate and pulsing frequency. Besides verifying the solids transfer technique and the method of bed pressure control assumed for the FBCR Miniplant design, the cold model studies permitted visual observation and measurement of the bed slugging characteristics that could be expected in the pilot unit when operating with the type of coarse lime particles for which it was designed.

The second phase of the program involved a study of the factors influencing the formation and the control of oxides of nitrogen (NO_x) in fluidized bed combustion. For these experimental studies, a 3 inch ID fluidized bed combustor and two smaller electrically heated fixed bed reactors were used. A fully instrumented analytical train permitted continuous measurement of NO, SO_2, CO and O_2 emissions. NO_2 emissions were found to be negligible. The operating factors that were studied included excess air level, bed temperature, and bed composition.

NO was found to react under fluidized bed combustion conditions with both CO and SO_2; the NO emission levels depended on the concentration of these components in the combustor. Unreacted lime and sulfated lime were found to catalyze the reduction of NO by CO with the unreacted material being the more active. Aluminum oxide (Alundum) also catalyzed the NO-CO reaction but was less active than $CaSO_4$. Based on very limited data, the NO-CO reaction appears to be second order in both NO and CO with an activation energy of only 6 to 8 Kcal/g-mole over the temperature range from 1300 to 1700°F. In the fluidized bed combustor, increasing the CO concentration by either decreasing the excess air level or decreasing the combustion temperature produced a decrease in NO emissions. Thus, with $CaSO_4$ (Drierite) as the bed

material, an oxygen level in the flue gas of 4%, and a superficial fluidizing velocity of 6 fps., NO emissions were 680 ppm at 1800°F and 560 ppm at 1500°F. At 1600°F, corresponding NO emissions were 650 ppm at 1% O_2 and 565 ppm at 8% O_2 in flue gas.

The data that were obtained on the NO-SO_2 reaction indicate that CaO is necessary for this reaction to proceed. In the absence of oxygen, fixed bed reactor data indicated an apparent reaction order of about 0.5 with respect to NO. This reaction has a negative temperature dependence, the apparent rate increasing by a factor of about five by decreasing the temperature from 1600°F to 1400°F. This decrease in rate was found to coincide with an increase in $CaSO_3$ thermodynamic stability, indicating that $CaSO_3$ is probably a reactant in this system.

A reactor configuration designed to yield low NO_x emissions by promoting the reduction of NO by CO and then the reaction of NO with SO_2 and lime was tested by modifying the 3 inch fluidized bed unit to permit its operation as a two stage combustor. In the first stage, operating at substoichiometric conditions, the NO-CO reaction would be promoted. The addition of secondary air at a higher point in the bed would complete the combustion and provide SO_2 for reaction with the remaining NO. Actual experiments confirmed these expectations. NO emissions were reduced from 615 ppm at 110 percent stoichiometric air and no staging to 200 ppm when 43% of the stoichiometric air was introduced through the grid in the first stage and 67% of the air at a point 6 inches above the grid.

INTRODUCTION

The fluidized bed combustion (FBC) of coal is being studied as a new boiler technique offering the potential of low SO_2 emissions by using limestone as the bed material. In FBC, the bed is kept fluidized by the combustion air and by the flue gas resulting from the combustion of the coal. High heat fluxes are achieved to the steam generating surface located in the bed permitting reduced tubing requirements in comparison to conventional boilers. The excellent heat transfer achieved in the bed, coupled with its high heat capacity, serves to maintain the fluidized bed boiler (FBB) temperature at a uniform level typically controlled in the range of 1500 to 1700°F. Other potential advantages of the FBB include reduced steam tube corrosion and fouling, and the ability to combust low quality fuels.

Within the FBB, limestone is calcined to lime which reacts with SO_2 and oxygen in the flue gas to form $CaSO_4$ as shown by reaction (1).

$$CaO + SO_2 + 1/2\ O_2 \longrightarrow CaSO_4 \qquad (1)$$

When used on a once-through basis, high limestone feed rates are required to the FBB if SO_2 removal of 90% or more is to be achieved.

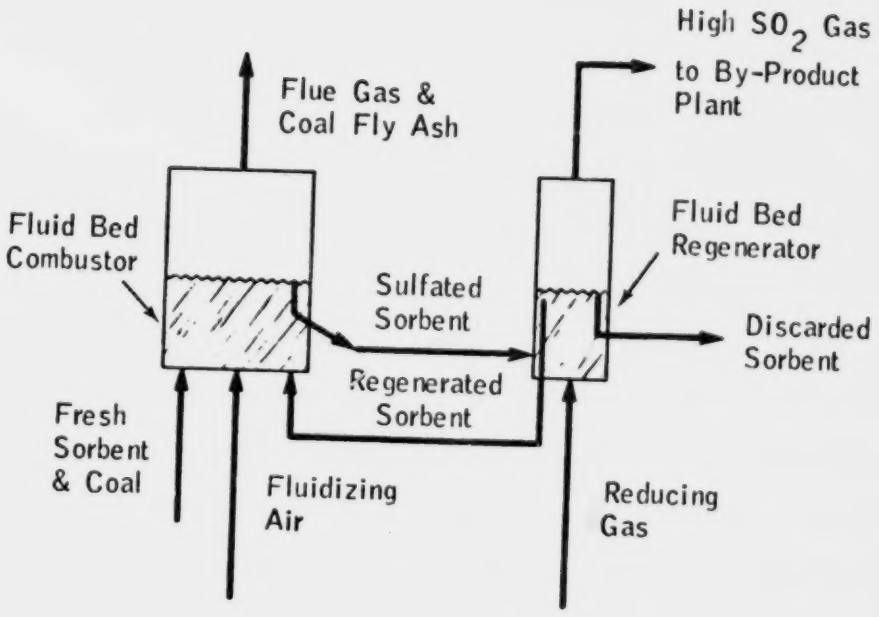
In order to reduce the solid waste disposal burden created by these high limestone feed rates, a system was proposed by Esso Research and Engineering Company in which the $CaSO_4$ would be regenerated back to

CaO in a separate fluidized bed reactor by reaction with a reducing gas at a temperature of about 2000°F.

$$CaSO_4 + \begin{Bmatrix} CO \\ H_2 \end{Bmatrix} \longrightarrow CaO + SO_2 + \begin{Bmatrix} CO_2 \\ H_2O \end{Bmatrix} \qquad (2)$$

The regenerated CaO would be returned to the FBB where it would again react with SO_2 and O_2.

Esso's Proposed Fluidized Bed
Combustion-Lime Regeneration System



In a study completed by Esso for the National Air Pollution Control Administration (1), the following essential features of the proposed regenerative-limestone FBB system were demonstrated:

- Removal of over 90% of the SO_2 formed by combusting coal in fluidized beds of lime.
- Reductive regeneration of the sulfated lime to yield an off-gas containing 7 to 12 mole % SO_2. This is a sufficiently high concentration to permit its conversion to H_2SO_4 or elemental sulfur with conventional technology.
- Good activity maintenance of the lime cycled back and forth between combustion and regeneration. The make-up requirement for fresh limestone in a commercial plant was estimated to be about 15% of that required for once-through use of this material.

These experimental results were obtained at atmospheric pressure conditions. Since completing this study, engineering and cost analyses carried out by Westinghouse (2) for the Environmental Protection Agency (EPA) have indicated a much greater commercial potential for a pressurized FBB system when used in conjunction with a combined gas-steam turbine power generating plant. Based on this evaluation, the Office of Air Programs of EPA requested Esso Research and Engineering Company to study the design of a continuous fluidized bed combustion-limestone regeneration pilot unit capable of operating at pressures up to 10 atmospheres. Part I of this report presents the results of this design study.

Besides its potential for controlling SO_2 emissions, the emissions of nitrogen oxides (NO_x) from FBC units were expected to be low because the low temperature at which the combustion occurs is unfavorable for the reaction of atmospheric nitrogen and oxygen. In fact, however, NO_x emissions are much higher than predicted from thermal equilibrium for atmospheric nitrogen fixation. Most of the NO_x formed in FBC results from the oxidation of the nitrogen organically bound in the coal. NO_x emissions depend on the extent of this oxidation and the subsequent reactions that the nitrogen oxides undergo in the fluidized bed.

As part of its program for the Environmental Protection Agency, Esso Research has investigated the effect of different FBC operating variables on the conversion of fuel nitrogen to NO. Subsequent reactions of NO with SO_2, CO, CaO and $CaSO_4$ have also been studied. The results of these studies are presented in Part II of this report.

PART I

DESIGN OF THE HIGH PRESSURE FLUIDIZED BED COMBUSTION LIME REGENERATION PILOT UNIT - THE FBCR MINIPLANT

This part of the report describes the design of the high pressure fluidized bed combustion-lime regeneration pilot unit (the FBCR Miniplant) that Esso Research and Engineering Company has prepared for the Office of Air Programs of EPA under Contract CPA 70-90. Previous studies by Esso (1) on the fluidized bed combustion-lime regeneration system had been conducted at atmospheric pressure in batch pilot unit equipment (see Part II - Section 1 for description of this equipment).

The design of the FBCR Miniplant involved three major steps:

(1) Selecting design conditions and operating parameters for the unit.

(2) Detailed design and engineering of the overall unit and its various sub-systems.

(3) Verification and modeling of critical design features.

In the following sections of this report, the FBCR Miniplant design is discussed in terms of these three steps.

1. DESIGN AND OPERATING PARAMETERS

The basis used for the design of the FBCR Miniplant is summarized in Table 1-1.

Table 1-1

Design Basis for the FBCR Miniplant

Maximum Operating Conditions	Combustor	Regnerator
Pressure (atm)	10	10
Temperature (°F)	1700	2000
Superficial Gas Velocity (ft/sec)	10	5
Unit Dimensions		
Internal Diameter (in.)	12	5
Height (ft)	28	19

The limiting operating conditions for the combustor were set at 10 atmospheres pressure, 1700°F bed temperature, and a superficial velocity of 10 fps. These maximum design conditions were based on the engineering and economic analyses that had been carried out by the Westinghouse Research Laboratories (2).

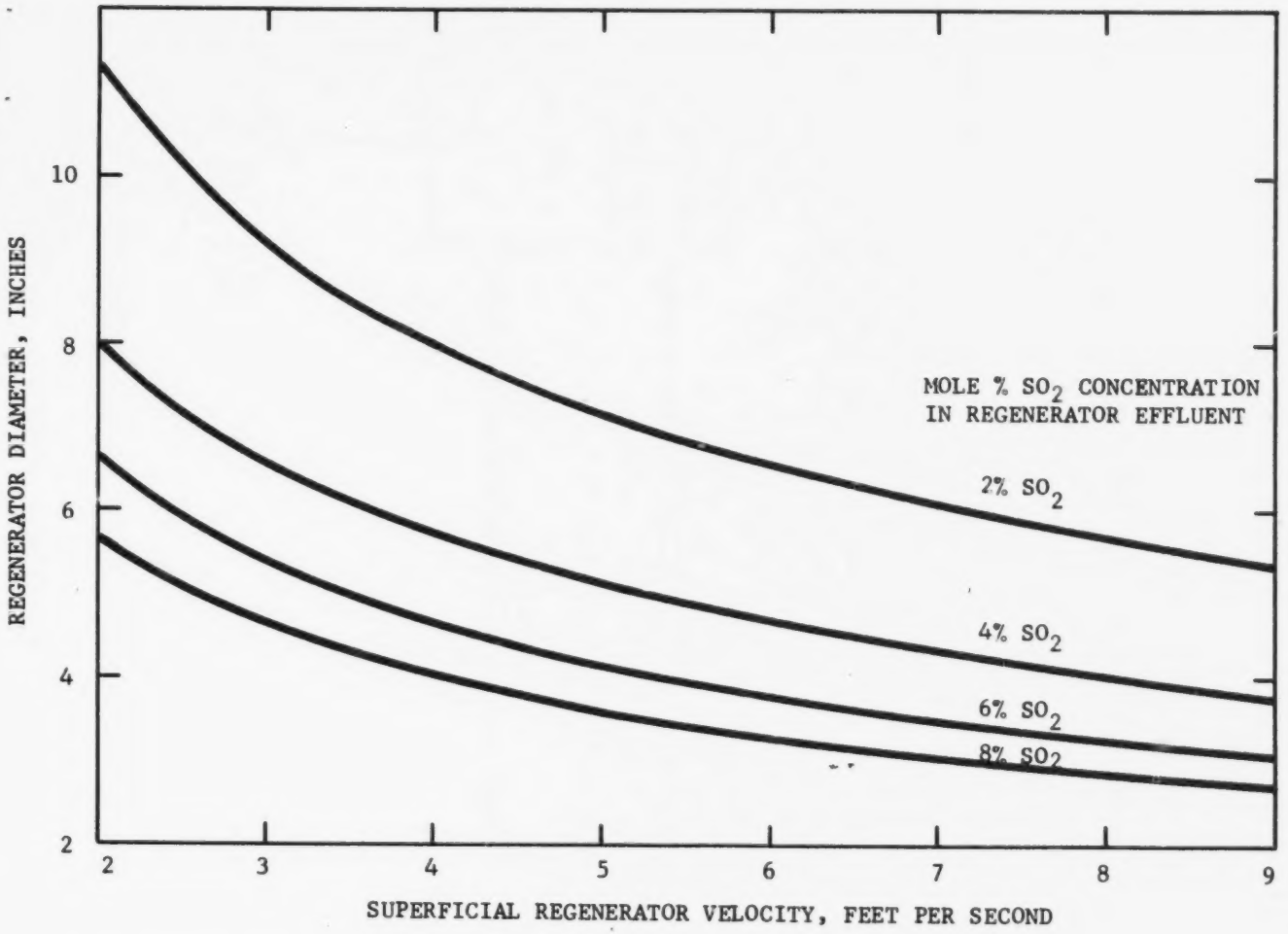
A 12-inch diameter combustor size was selected as a basis for design because this would provide a system which could be constructed at reasonable cost and within reasonable time while still providing the essential data needed for future development of the pressurized FBC system. At the design conditions, a maximum coal feed rate of 482 lbs. per hour would be possible when operating the combustor with 15% excess air. With a heating value of about 13,000 BTU/lb, this coal rate would correspond to a heat release rate of 6.3×10^6 BTU/hr.

The internal diameter and operating velocity of the regenerator were the next parameters to be specified. As shown in Figure 1-1, these are not independently adjustable parameters. They are related to each other and to the diameter and operating velocity of the combustor by a sulfur material balance over the system. A critical factor in this balance is the SO_2 concentration of the regenerator off-gas. Since no experimental data on pressurized regeneration were available, it was necessary to assume a value for the SO_2 concentration in the design of the FBCR Miniplant. An assumed value of 4 mole % SO_2 in the regenerator off-gas was used for this purpose. This is a conservative value based on thermodynamic calculations that were made and which are summarized in Appendix 1. Using the 4 mole % SO_2 concentration as the basis, a 5 inch diameter reactor and a 5 fps superficial velocity was selected from the curves shown in Figure 1-1 as representing the best compromise for the design of the FBCR Miniplant.

A material balance for the designed FBCR Miniplant operating at its maximum design coal throughput is shown in Figure 1-2.

FIGURE 1-1

RELATIONSHIP BETWEEN REGENERATOR
DIAMETER AND OPERATING VELOCITY



Above curves have been developed from the equation:

$$\frac{T_R}{T_C} \cdot \frac{C_C^{SO_2}}{C_R^{SO_2}} \cdot V_C D_C^{\,2} = V_R D_R^{\,2}$$

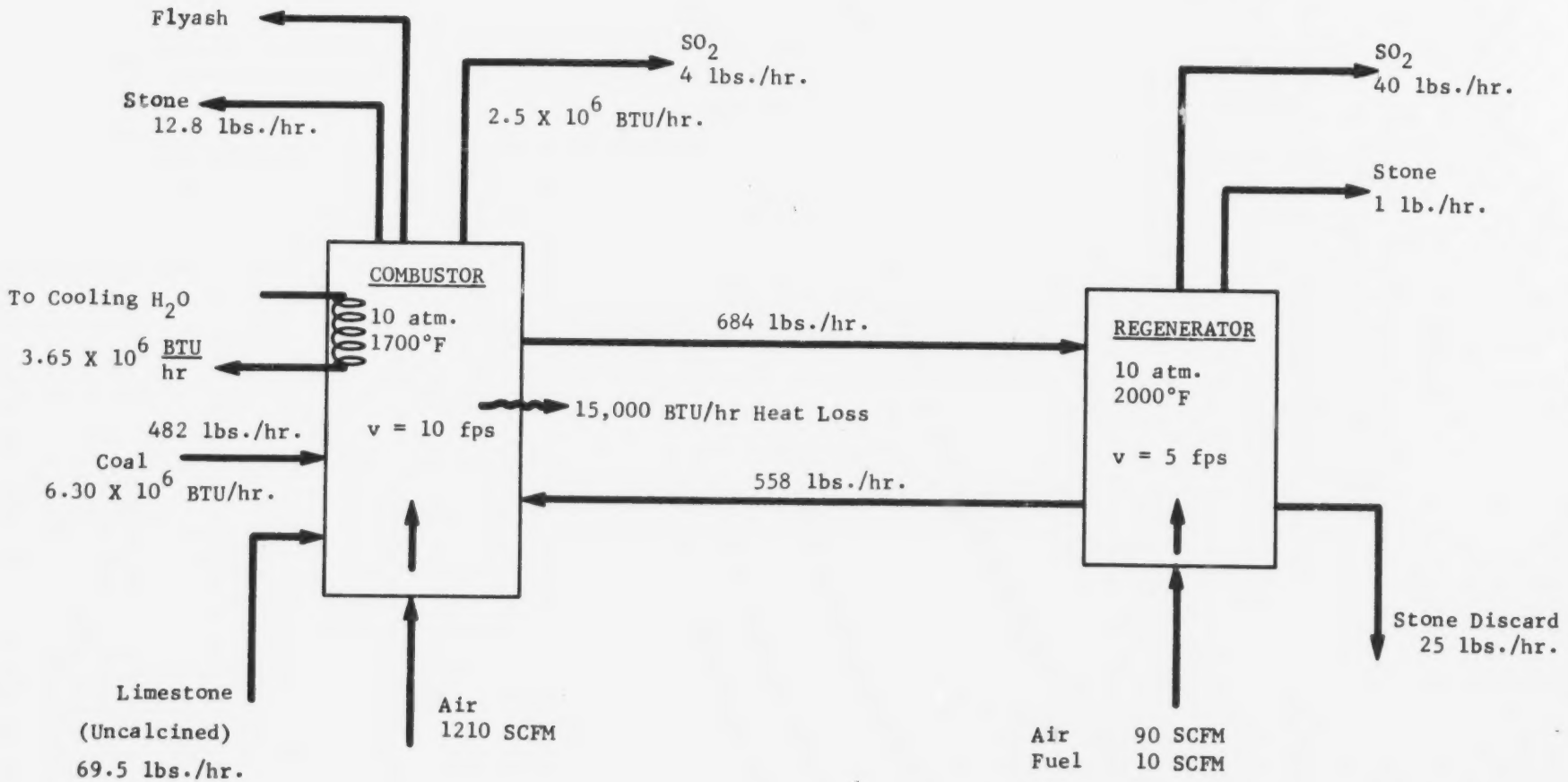
which is based on a SO_2 material balance between the combustor and regenerator. In this equation,

T = Absolute temperature
C^{SO_2} = SO_2 concentration (based on S content of coal for the combustor)
V = Superficial velocity
D = Reactor diameter

and the subscripts refer to the regenerator conditions (R) and the combustor conditions (C)

FIGURE 1-2

MATERIAL BALANCE FOR THE FBCR MINIPLANT



Basis: 15% Excess Air
4.5% Sulfur Coal
1:1 Ca/S Ratio

2. THE FBCR MINIPLANT DESIGN

Figure 1-3 shows the overall system flow plan for the FBCR Miniplant and Figure 1-4 the assembly drawing for it.

Main fluidizing air for the combustor and regenerator is supplied at operating pressures to 125 psig by a stationary compressor with a capacity of 1300 SCFM. The air flow rates are measured by orifice flow meters and regulated by differential pressure transmitters and control valves. The superficial bed velocity in the combustor and regenerator can be controlled automatically and independently in this manner. In the combustor, the air passes through the distributing grid, up through the fluidized bed of solids, and out through two stages of cyclone for solids removal before it is cooled in a heat exchanger. The pressure in the combustor is maintained at a desired set point by a butterfly valve in the exhaust line positioned by a pressure transmitter and controller.

Air for the regenerator can be electrically preheated for temperature control before passing into the reducing gas generator located at the bottom of the reactor. The reducing gas passes through a ceramic distributor plate which supports the fluidized bed. The exit gas from the regenerator is cooled by a heat exchanger before discharging through a butterfly valve. The pressure is the regenerator is maintained about equal to the pressure in the combustor by a differential pressure transmitter and controller between the combustor and regenerator serving to position the butterfly valve in the regenerator discharge line.

FIGURE 1-3

FBCR MINIPLANT FLOW PLAN

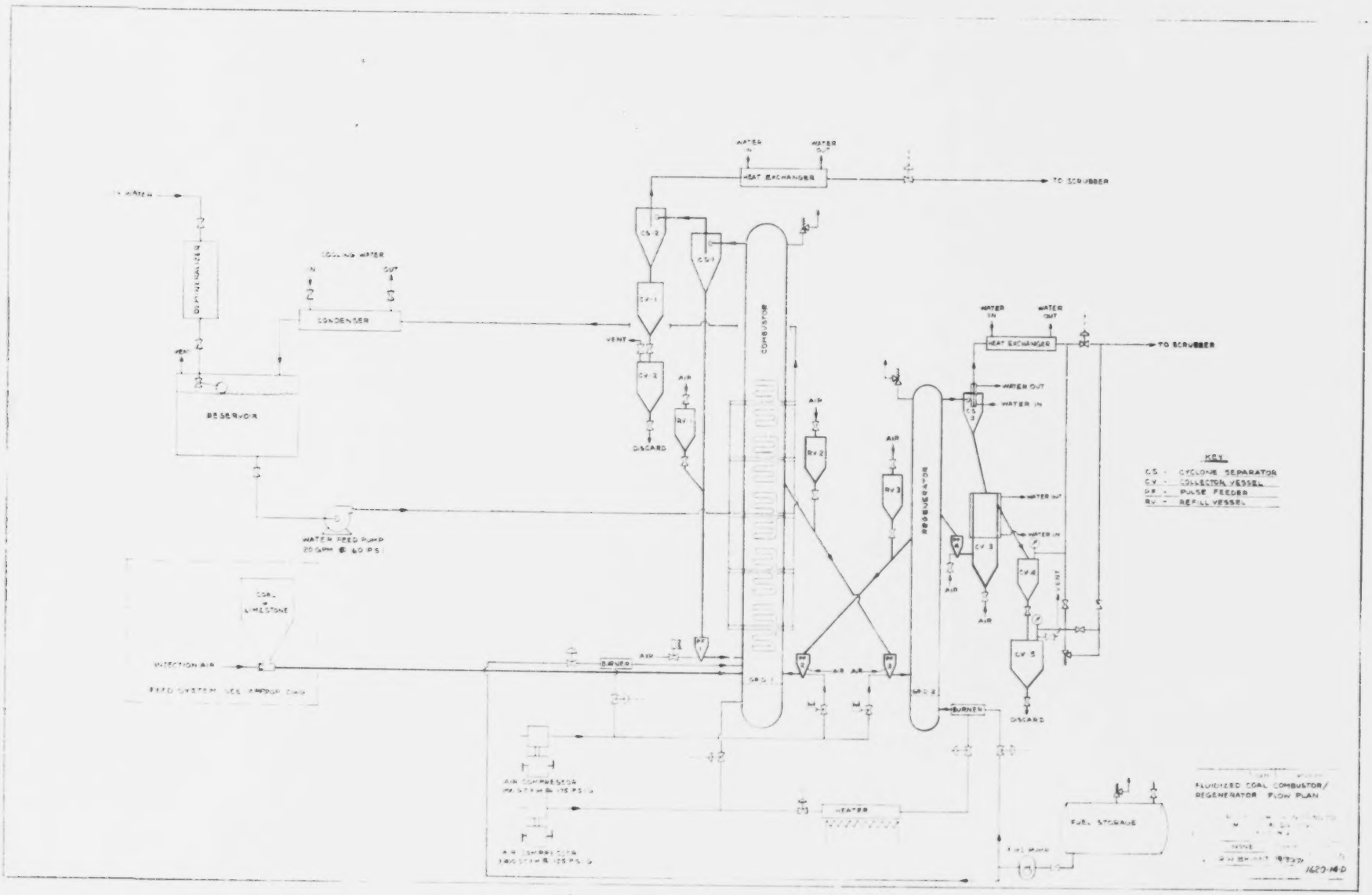
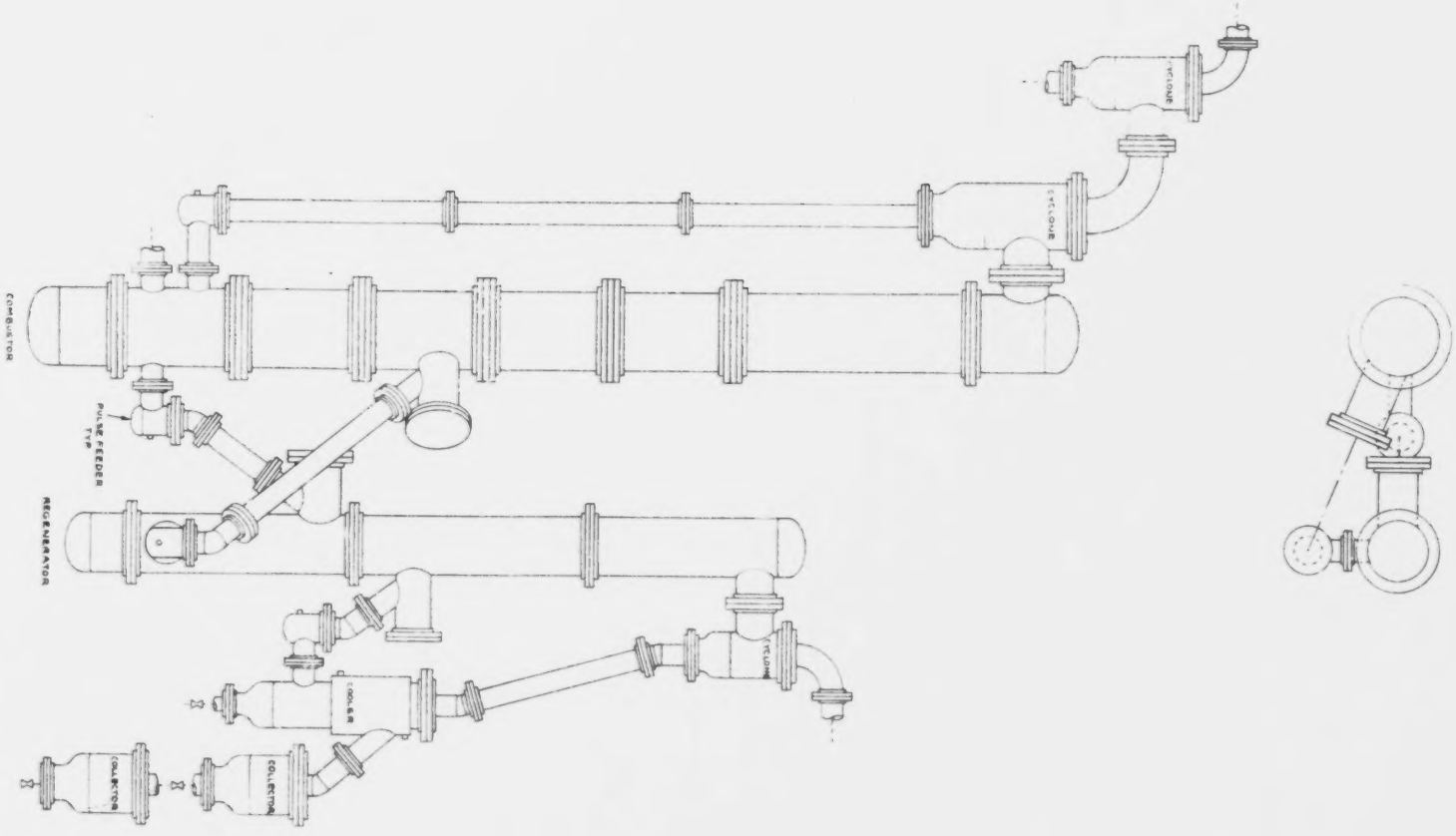


FIGURE 1-4

FBCR MINIPLANT ASSEMBLY



	DATE	REVISIONS
FLUIDIZED COAL COMBUSTOR REGENERATOR - ASSEMBLY		
ESSO RESEARCH AND ENGINEERING CO MECHANICAL DIVISION UNDER W.O.		
SCALE 3/8" = 1'	DATE	SHEET
G W BRIANT 10/4/71		DWG NO 1629-13 D

Heat extraction and temperature control in the fluidized bed combustor is accomplished by boiling demineralized water in 10 separate loops located in discrete vertical zones of the reactor. The water flow to these loops is controlled by valves whose positions automatically change to maintain bed temperature. The steam generated in these loops is condensed and returned to a reservoir.

Solids transfer between reactors, and discharge of solids from the system (i.e., the regenerator reactor) are accomplished using a pulsed air transport technique controlled by pressure differentials across and between these fluidized beds. Coal and makeup limestone to the combustor are fed continuously from a system designed for controlled solids feeding under pressure.

2.1 Combustion and Regeneration Reactors

The combustion and regeneration reactors constitute the heart of the FBCR Miniplant design. The combustor (see Figures 1-5, 1-6) consists of a 24-inch steel shell refractory lined to an actual internal diameter of 12.5 inches. The overall height of 28 feet was chosen to provide a bed outage (i.e., dilute phase above the bed) at least equal to the expanded bed height that would be obtained at the maximum operating conditions. The reactor is designed in flanged sections, with a bottom plenum for the combustion air, and an upper section for discharging the flue gas to the cyclones.

The regenerator reactor (see Figures 1-7, 1-8) consists of an 18-inch shell refractory lined to 5-inches internal diameter. An overall reactor height of 19 feet provides for bed expansion and reactor outage.

FIGURE 1-5

COMBUSTOR SHELL

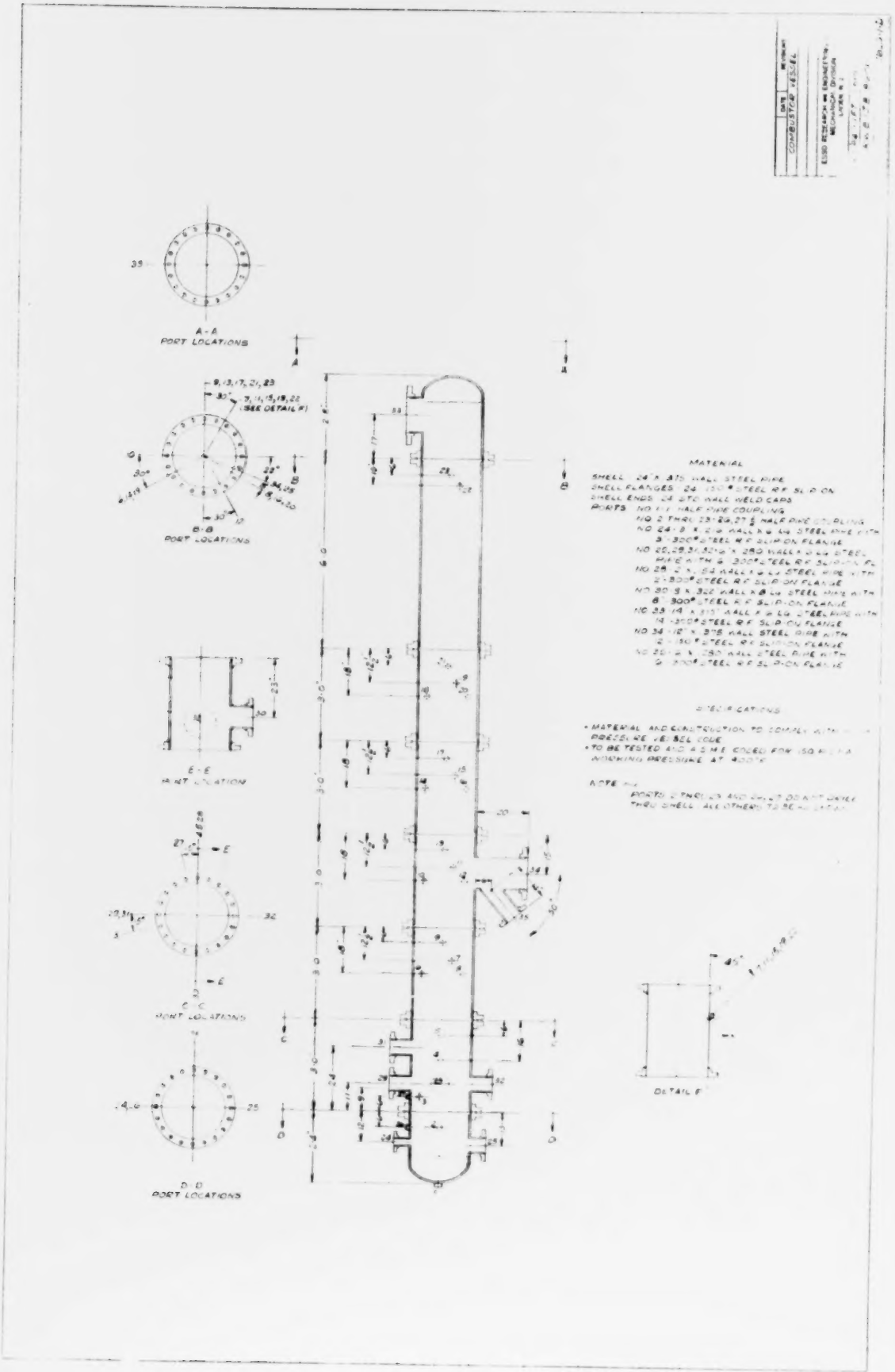

A-A
PORT LOCATIONS
B-B
PORT LOCATIONS
E-E
PORT LOCATIONS
C-C
PORT LOCATIONS
D-D
PORT LOCATIONS
DETAIL F
MATERIAL
SHELL - 24" X .375 WALL STEEL PIPE
SHELL FLANGES - 24" 150 # STEEL R.F. SLIP ON
SHELL ENDS - 24" X .75 WALL WELD CAPS
PORTS - NO. 1 - 1" HALF PIPE COUPLING
NO. 2 THRU 23 - 28, 27 & 1" HALF PIPE COUPLING
NO. 24 - 8" X .219 WALL X 8" LG. STEEL PIPE WITH 8" 300# STEEL R.F. SLIP ON FLANGE
NO. 25, 26, 31, 32 - 6" X .280 WALL X 6" LG. STEEL PIPE WITH 6" 300# STEEL R.F. SLIP ON FLANGE
NO. 29 - 2" X .154 WALL X 4" LG. STEEL PIPE WITH 2 - 300# STEEL R.F. SLIP ON FLANGE
NO. 30 - 8" X .322 WALL X 8" LG. STEEL PIPE WITH 8" 300# STEEL R.F. SLIP ON FLANGE
NO. 33 - 14" X .375 WALL X 8" LG. STEEL PIPE WITH 14" 300# STEEL R.F. SLIP ON FLANGE
NO. 34 - 12" X .375 WALL STEEL PIPE WITH 12" 300# STEEL R.F. SLIP ON FLANGE
NO. 35 - 6" X .280 WALL STEEL PIPE WITH 6" 300# STEEL R.F. SLIP ON FLANGE
SPECIFICATIONS
• MATERIAL AND CONSTRUCTION TO COMPLY WITH ... PRESSURE VESSEL CODE
• TO BE TESTED AND A.S.M.E. COLED FOR 150 PSI A WORKING PRESSURE AT 400°F
NOTE ...
PORTS 2 THRU 23 AND 27 DO NOT DRILL THRU SHELL. ALL OTHERS TO BE ...
COMBUSTOR VESSEL
ESSO RESEARCH AND ENGINEERING
MECHANICAL DIVISION

FIGURE 1-6

REFRACTORY LINED COMBUSTOR

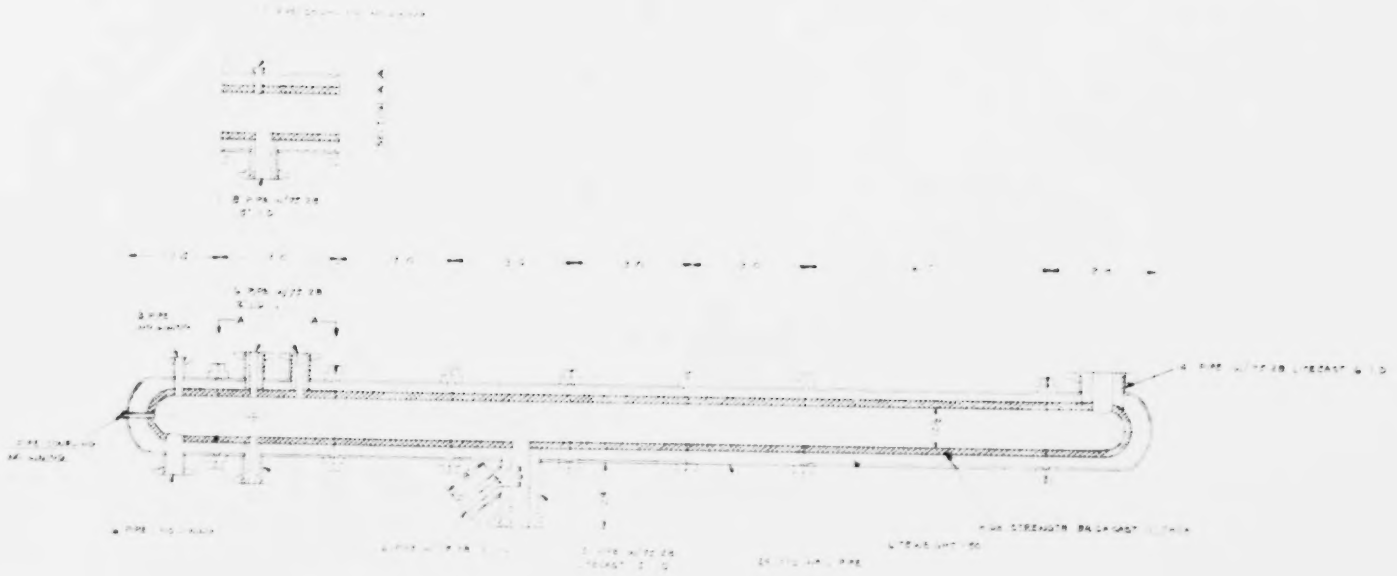


FIGURE 1-7

REGENERATOR SHELL

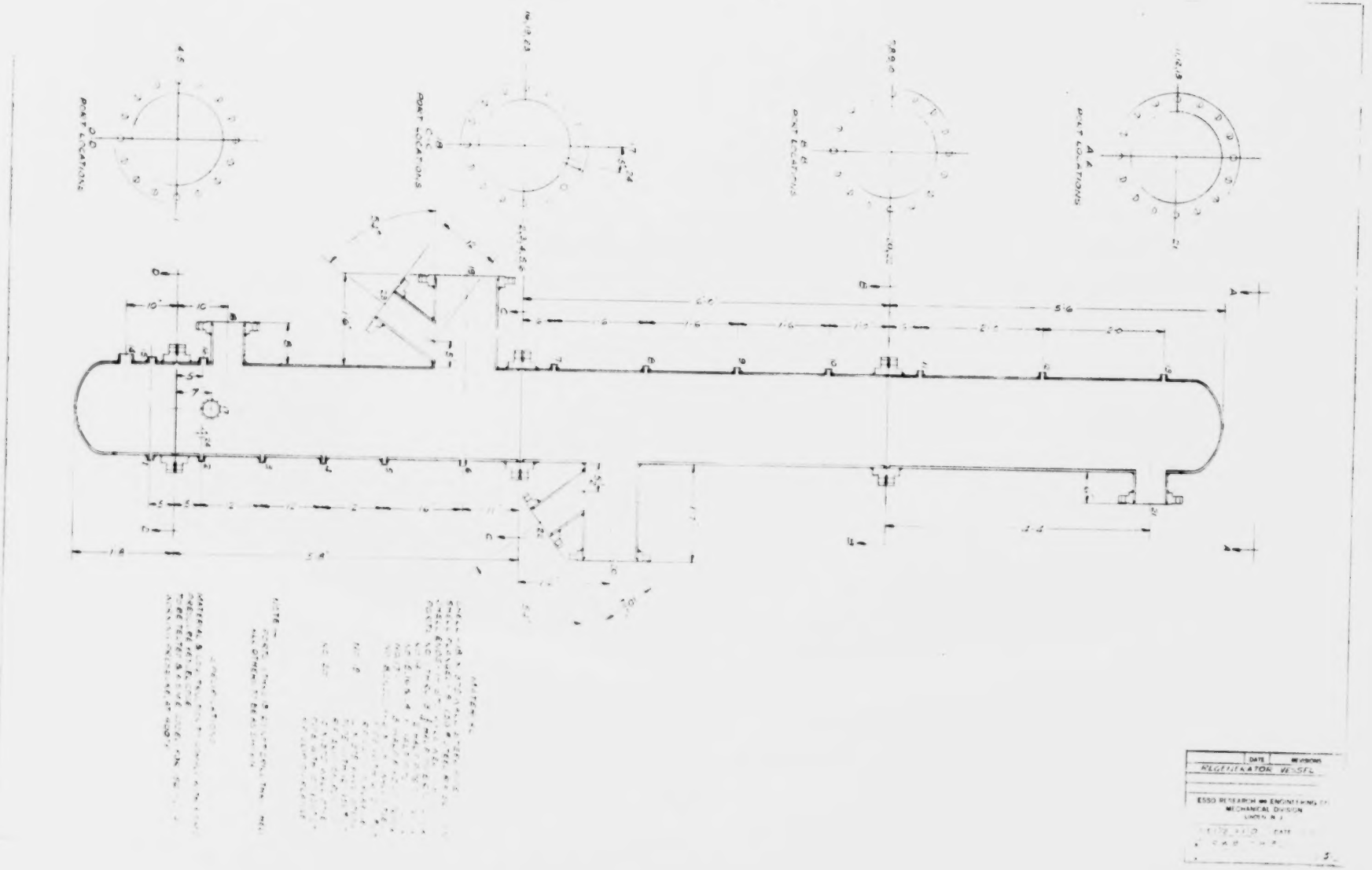
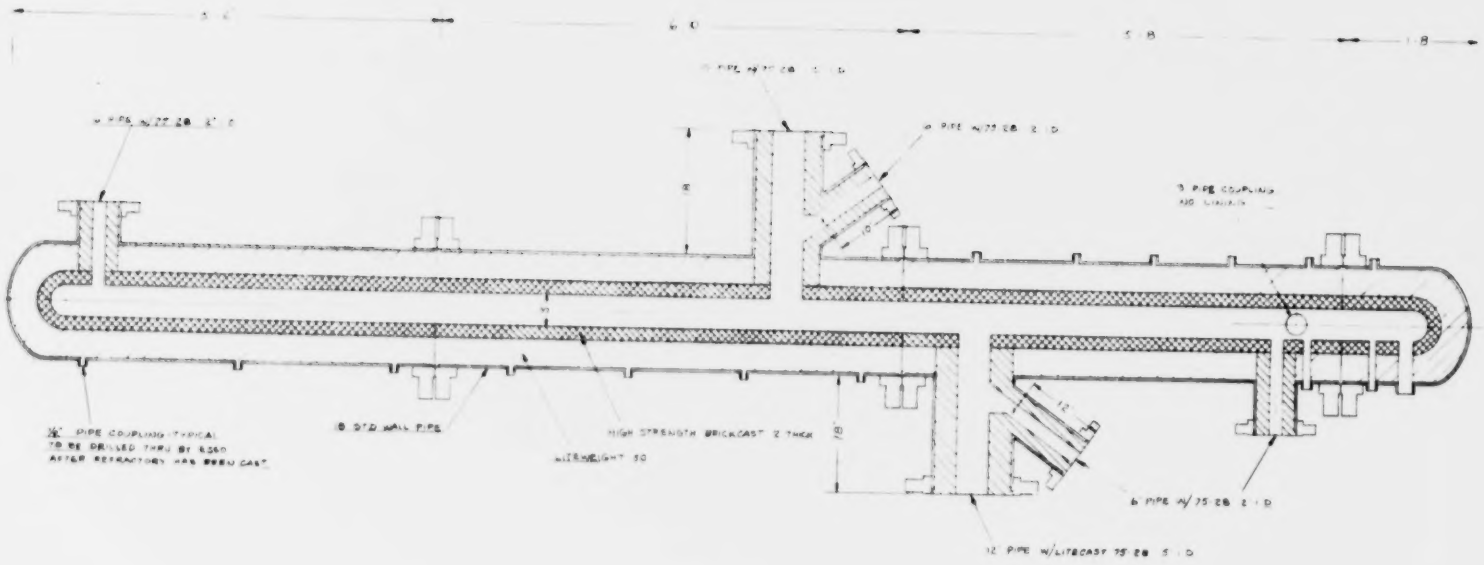


FIGURE 1-8

REFRACTORY LINED REGENERATOR



2.2 Bed Support and Gas Distribution Grids

Figure 1-9 provides the details of the combustor grid design. This grid consists of 3/8 inch stainless steel plate containing 137 fluidizing nozzles on a 15/16 inch square pitch. Each of the 5/8 inch diameter fluidizing nozzles contains 8 horizontal equally-spaced 5/64 inch holes. The combustor grid has been designed to provide a pressure drop of about 19 inches of H_2O.

The regenerator grid is a high alumina porous ceramic plate that will be sandwiched between the flanges of the main regenerator and the bottom plenum. Plate porosity will be picked to give a pressure drop close to that of the combustor grid.

2.3 Cyclones and Discharge System

In the FBCR Miniplant design, flue gases and entrained solid particles from the combustor enter a two-stage cyclone separator system (Figure 1-10). The solid particles separated in the first stage cyclone are returned to the combustor near the grid via a dip leg extension pipe. Solids escaping the primary cyclone enter the more efficient second stage cyclone where they are separated and discarded by means of a lock hopper system (Figure 1-13: two such vessels in series). This technique permits the selective removal of fly ash and limestone fines from the system on a continuous basis.

Gas exiting from the regenerator enters a single stage cyclone (Figure 1-11) where the entrained particles are collected and discarded by means of a two-vessel discharge system (Figures 1-12 and 1-13). All cyclones are lined with refractory insulation and rated for operation at pressures to 10 atmospheres.

FIGURE 1-9

COMBUSTOR AIR DISTRIBUTOR PLATE

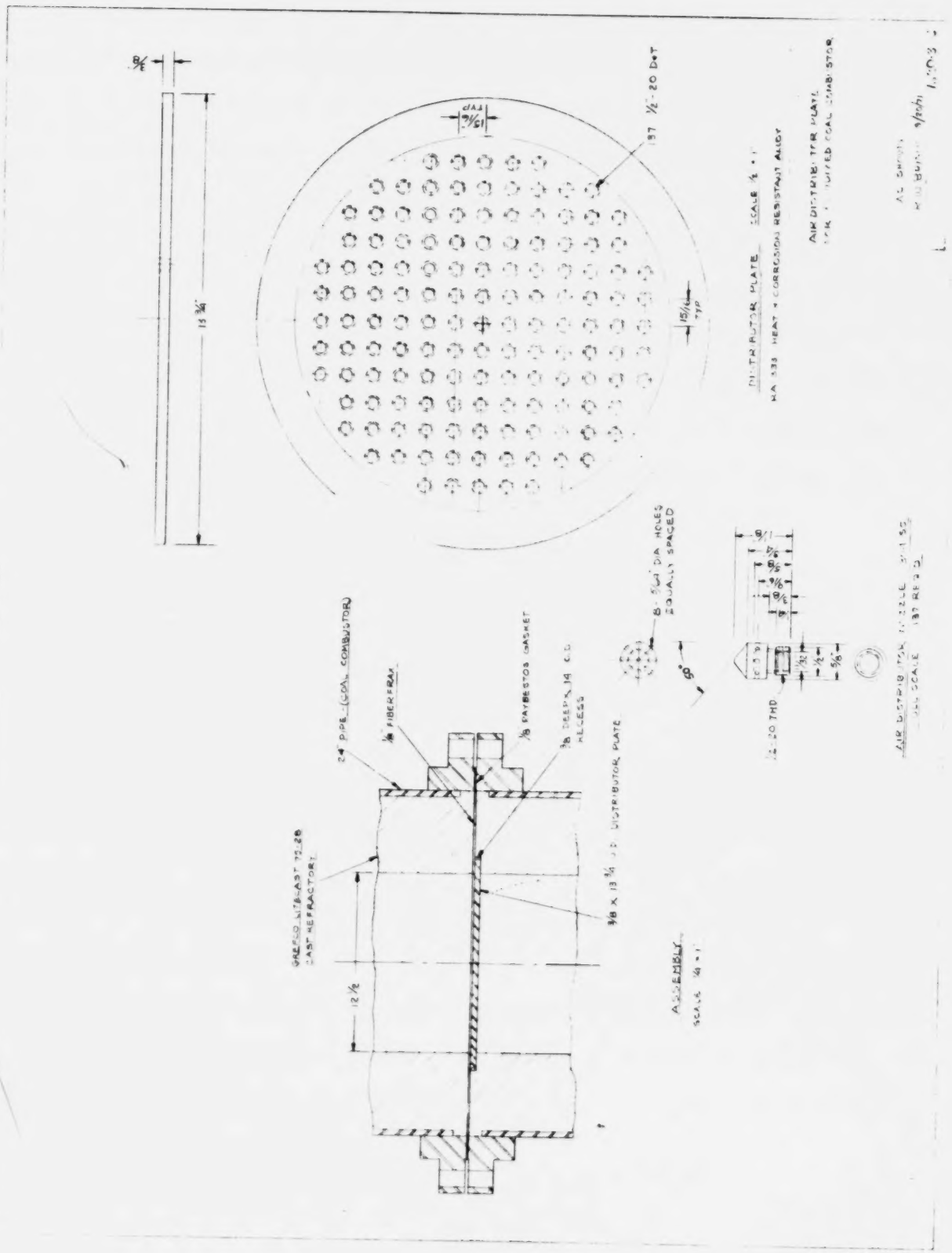


FIGURE 1-10

COMBUSTOR CYCLONE

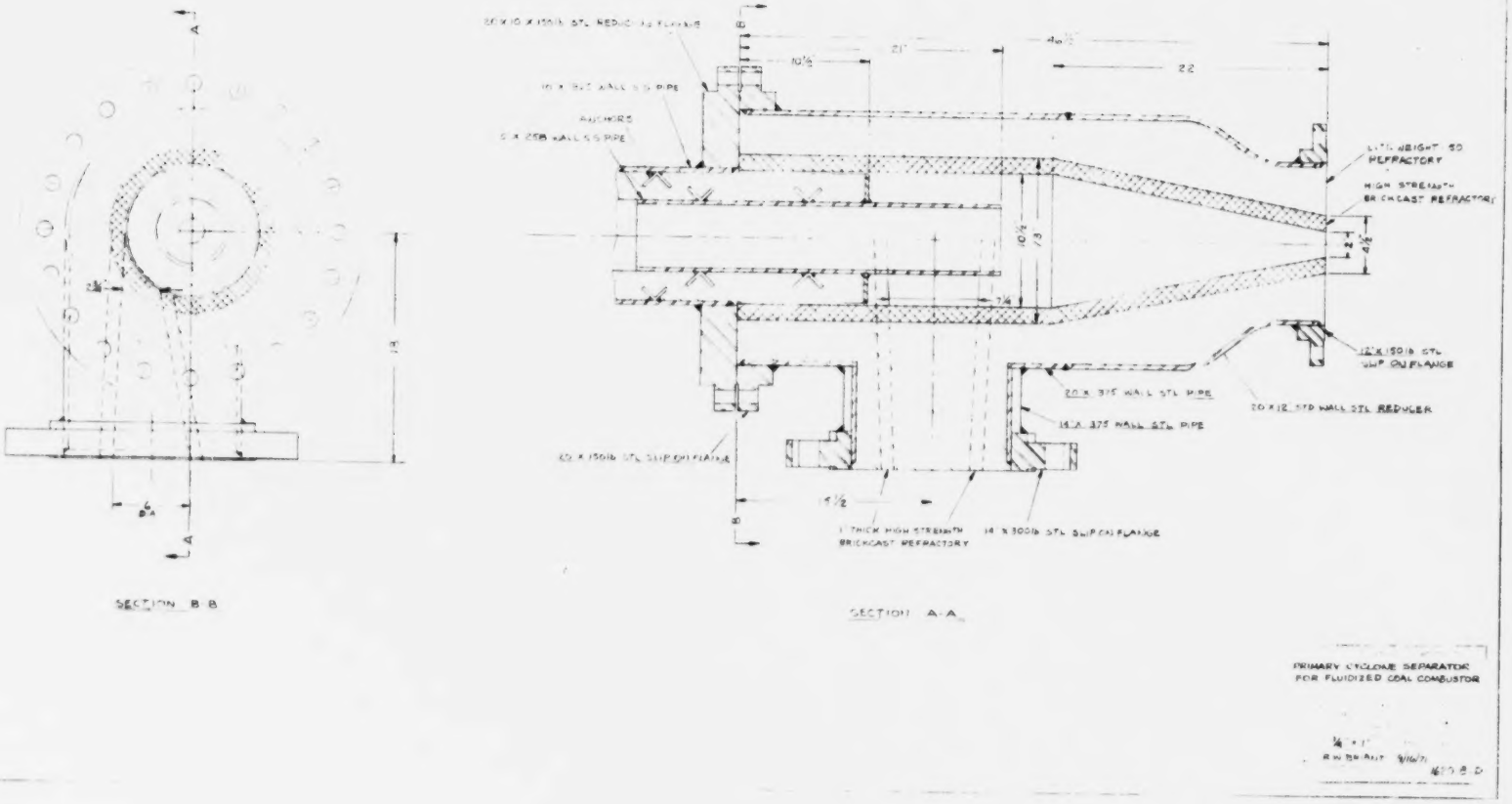


FIGURE 1-11

REGENERATOR CYCLONE

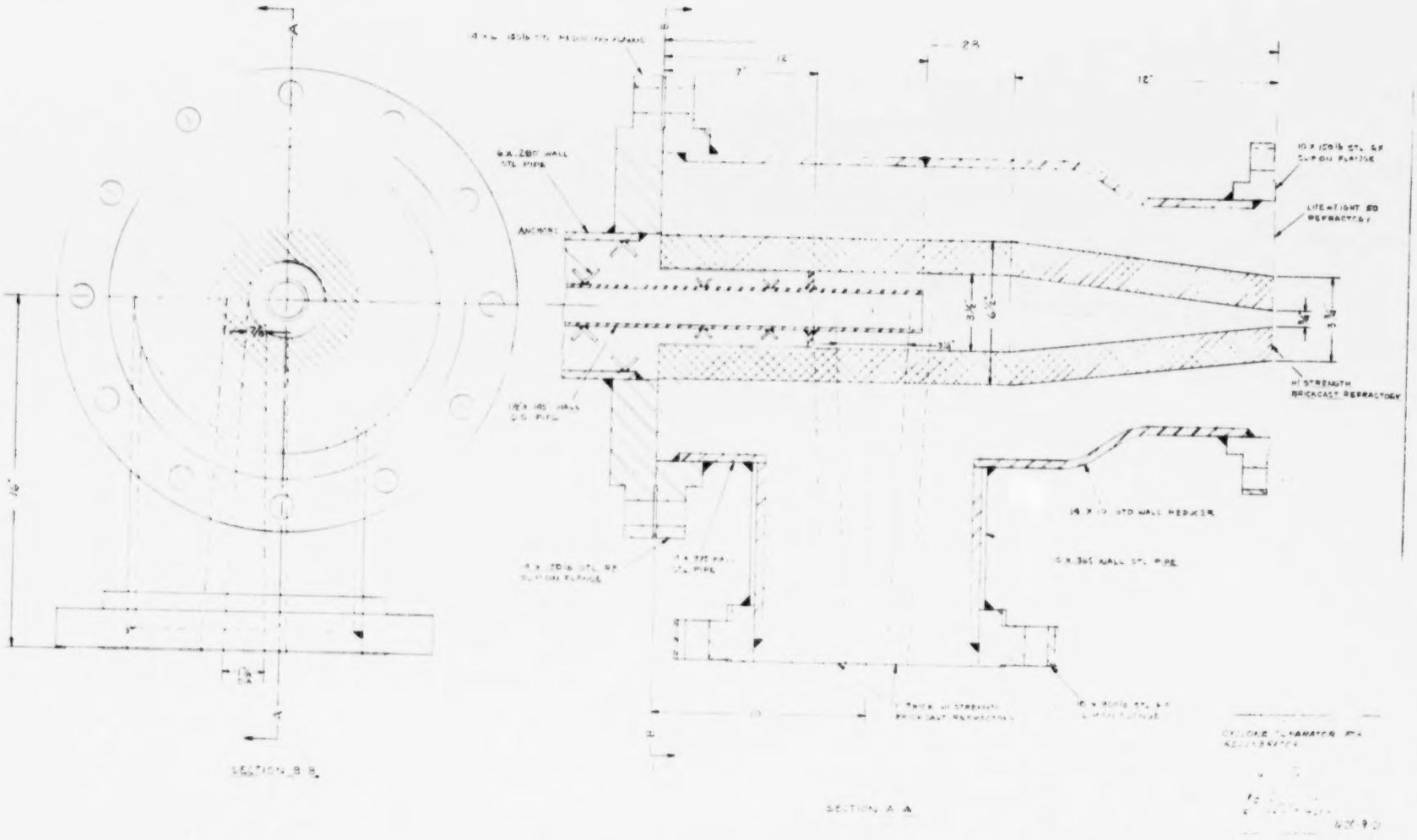

LITE WEIGHT ISO REFRACTORY
HI STRENGTH PRECAST REFRACTORY
14 X 10 STD WALL REDUCER
6 X 36S WALL STL PIPE
SECTION B-B
SECTION A-A

FIGURE 1-12

RECEIVER VESSEL #1

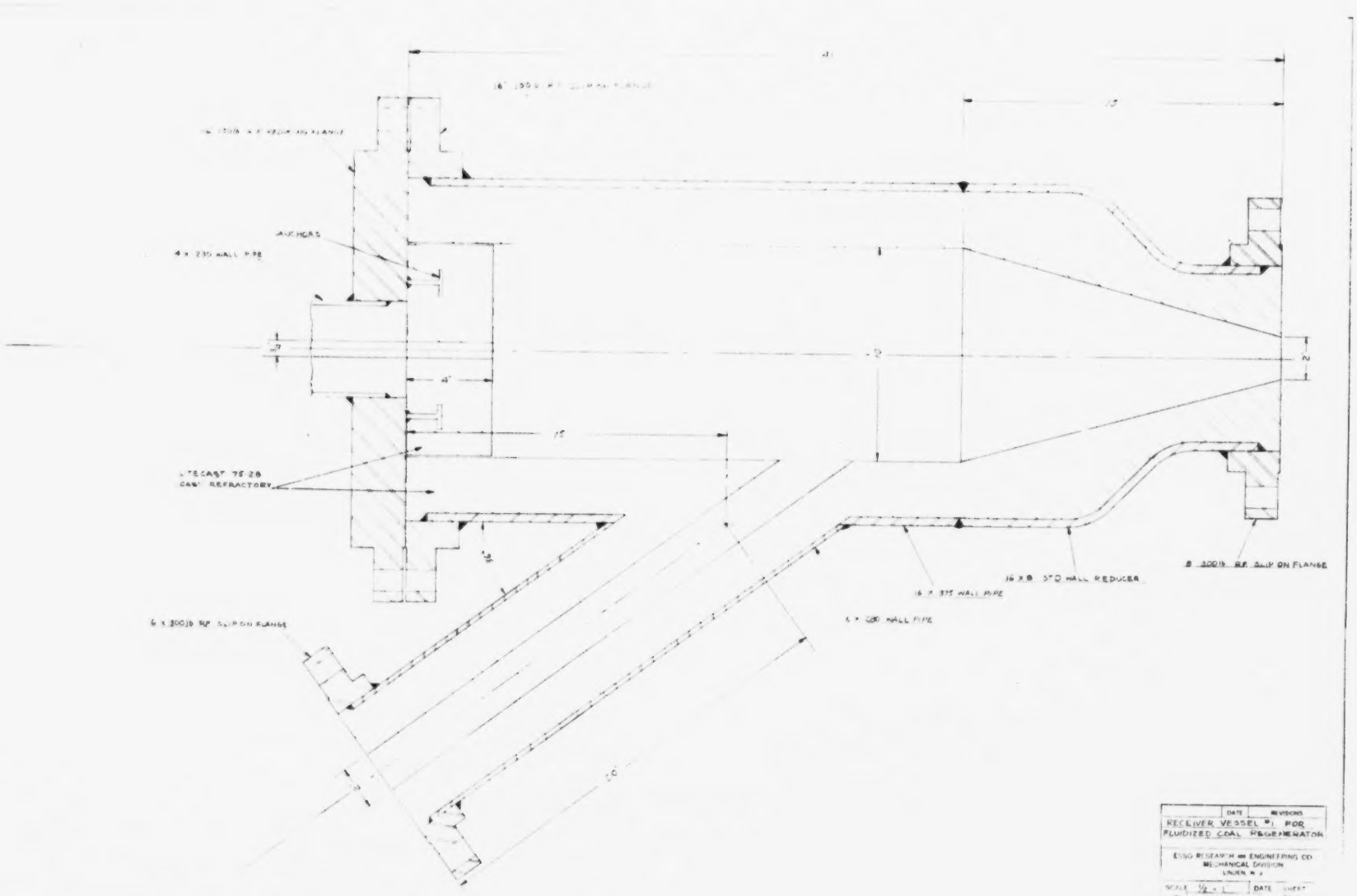
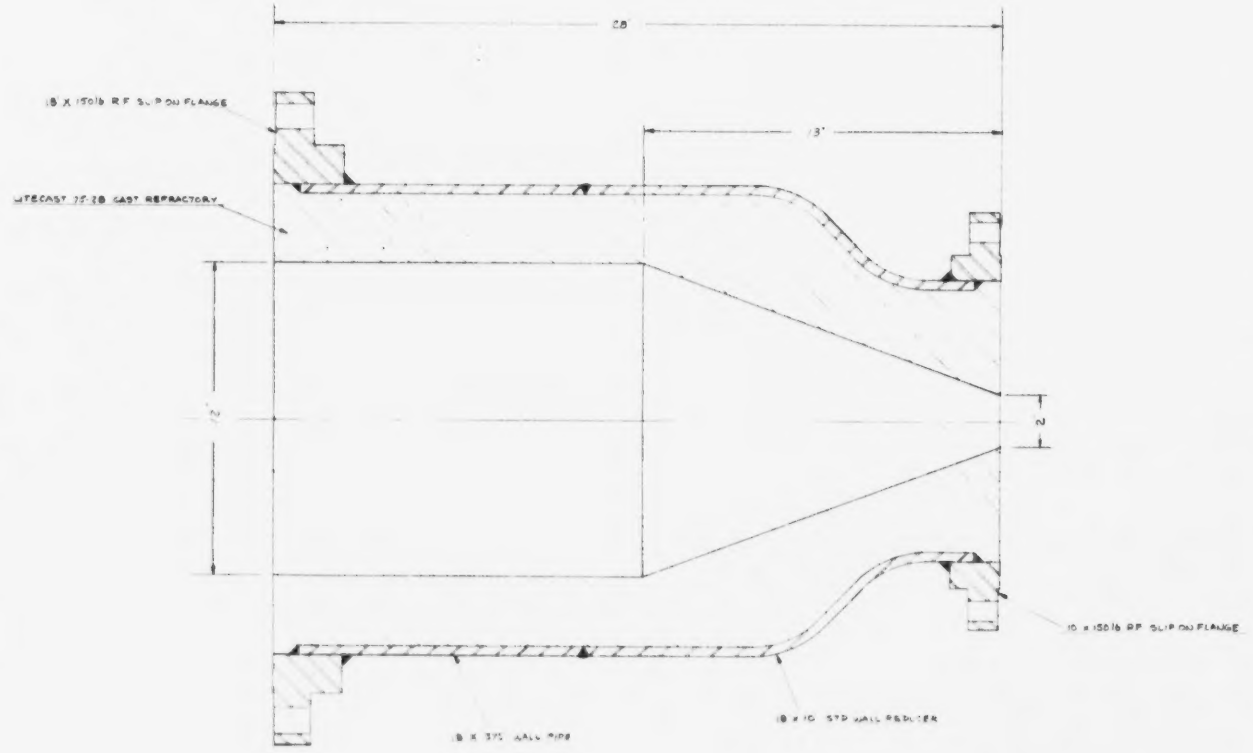


FIGURE 1-13

RECEIVER VESSEL #2


28
18 X 150lb R.F. SLIP ON FLANGE
13'
LITECAST 75-28 CAST REFRACTORY
2
18 X 3/8 WALL PIPE
18 X 10 STD WALL REDUCER
10 x 150lb RF SLIP ON FLANGE

RECEIVER VESSEL #2 FOR REGENERATOR

1623-12-2

Discharge gases from the cyclones are cooled in heat exchangers to reduce the exit gas temperatures. This minimizes the need for refractory lined pipe leading to the scrubber, and lowers the temperature rating required for the reactor back pressure control valves.

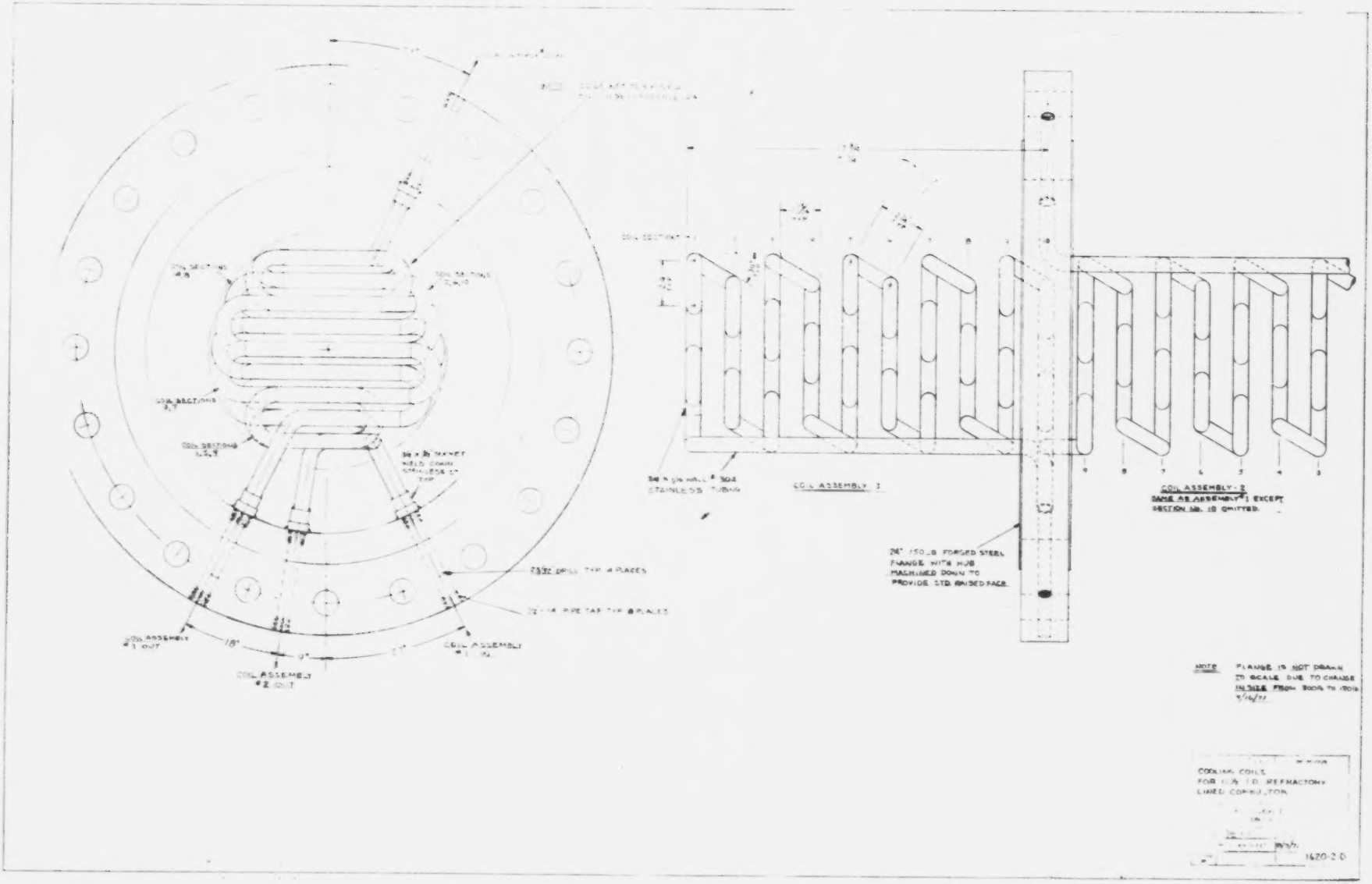
2.4 Combustor Heat Removal

At the maximum operating conditions for which the FBCR Miniplant has been designed, a combustor cooling load of approximately 3.6×10^6 BTU/hr is required to maintain a 1700°F bed temperature. With the design calling for a 15 foot expanded bed height, 240,000 BTU/hr/ft of bed must be removed. The design that has been developed for this purpose calls for control of bed temperature by water circulation through 10 individual serpentine tube loops located in discrete vertical zones of the expanded bed. Each loop occupies 18 inches of bed height and consists of 3/4 inch boiler tubes on a 2-1/4 inch horizontal pitch (Figure 1-14). The coolant enters and exits the combustor through 5 special coolant distributor plates sandwiched between flanges at 3 foot vertical increments in the lower portion of the reactor. This arrangement obviates penetrating the refractory lined shell of the reactor and provides a means of combustor disassembly for inspection and maintenance.

The combustor cooling water is pumped from a feedwater storage tank through the tube loops, where a portion of it is vaporized. The liquid-vapor mixture then flows through a surface condenser where it is condensed and returned to the feedwater tank. Thus, the steam and saturated water generated in the combustor cooling tubes is condensed, cooled and

FIGURE 1-14

COMBUSTOR COOLING COILS


COIL ASSEMBLY #1 OUT
COIL ASSEMBLY #2 OUT
COIL ASSEMBLY #1 IN
COIL ASSEMBLY 3
COIL ASSEMBLY #2
SAME AS ASSEMBLY #1 EXCEPT SECTION No. 10 OMITTED.
STAINLESS TUBING
26" 150 LB FORGED STEEL FLANGE WITH HUB MACHINED DOWN TO PROVIDE STD. RAISED FACE
NOTE FLANGE IS NOT DRAWN TO SCALE DUE TO CHANGE IN SIZE FROM 300# TO 150#
9/16/71
COOLING COILS
1620-20

recirculated to the combustor to maintain a clean, closed cooling water system. The fresh make-up water required is demineralized before entering the feedwater storage tank. This recirculating arrangement is intended to minimize cooling tube fouling, thereby maintaining effective heat transfer and extended tube life.

2.5 Coal and Limestone Preparation and Injection

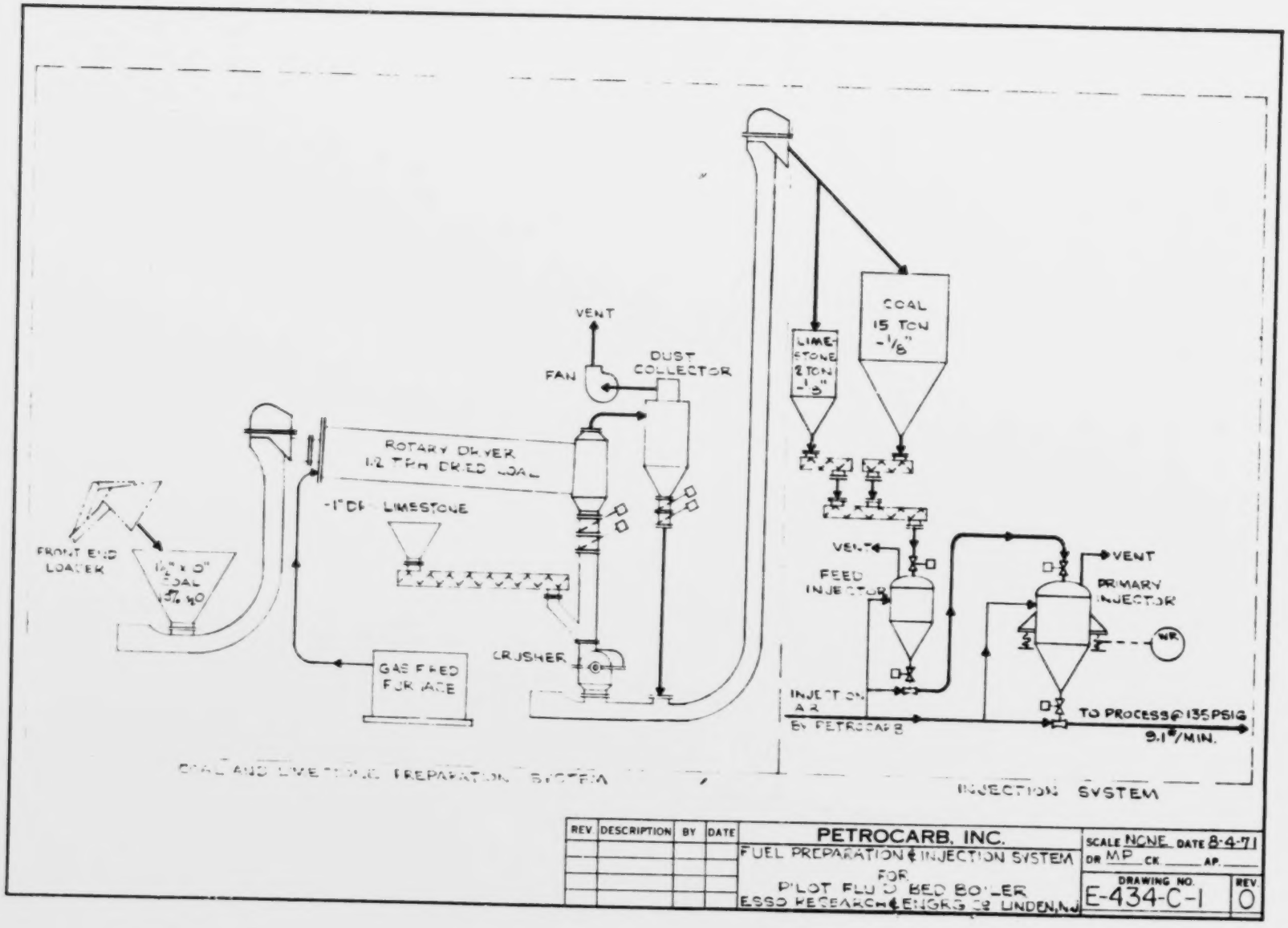
The design of the coal and limestone preparation and injection system for the FBCR Miniplant has been provided by Petrocarb Inc. (Figure 1-15). Petrocarb claims this system to be capable of continuously processing and feeding the required mixture of coal and limestone to the combustor at a rate of 550 lbs/hr against a combustor pressure of 10 atmospheres. The preparation system dries and crushes the coal to a minus 1/8 inch size injection quality and delivers the crushed coal to a storage bin.

Coal is taken as received from an existing pile by a front end loader and placed in the system hopper from which it is fed to a rotary dryer for drying to 1% maximum moisture. Dryer heat is furnished by a gas fired hot air furnace, and the moisture laden exhaust gases are vented by an exhaust blower through a cyclone dust collector and then to the atmosphere. The collected dust particles become part of the processed product.

Dried coal discharges from the dryer into the crusher where it is reduced to minus 1/8 inch size. It is then conveyed to a 15 ton coal storage bin. Limestone can be processed in the same manner in a subsequent operation, and stored in an adjacent 2 ton capacity limestone storage bin.

FIGURE 1-15

COAL/LIMESTONE FEEDING SYSTEM



Volumetric feeders deliver coal and limestone in the ratio of approximately 5 to 10 parts of coal to 1 part limestone from their respective storage bins to a blender and then to a feed injector vessel. This mixture of coal and limestone is then transferred pneumatically to the primary injector vessel upon a demand weight signal from the primary injector.

After the charge is transferred from the feed injector to the primary injector, the feed injector is isolated, vented and refilled in preparation of a new weight demand signal from the primary injector. The weight cell on which the primary injector is mounted is also used to monitor the materials feed rate to the combustor.

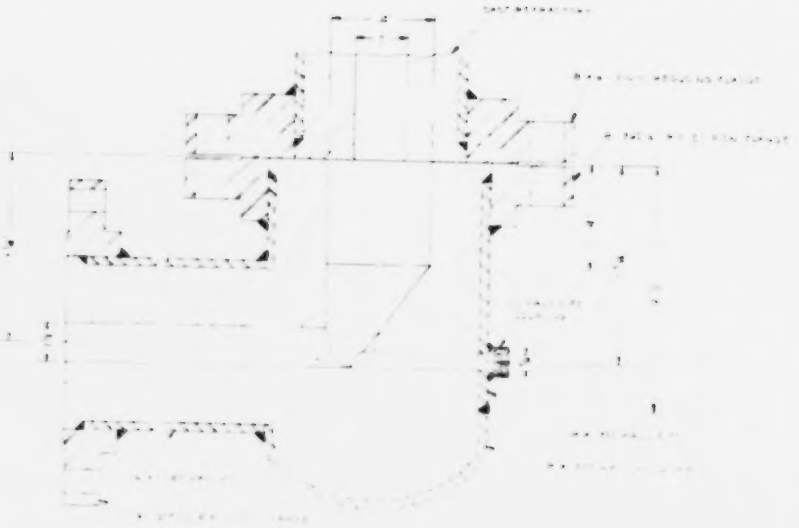
Aerated solids in the primary injector gravity flow through an orifice into a mixing section where a controlled air stream transports them into the combustor. The solids feed rate is controlled by the transport air flow rate and the pressure. Thus, under emergency conditions, the coal supply to the combustor can be stopped by cutting off the injection air stream.

2.6 Solids Transfer

Stone is continuously transferred from the combustor to the regenerator and from the regenerator to the combustor by inducing the solids to surge into an overflow reservoir immersed in the upper expanded bed of the reactor (See Figures 1-6 and 1-8). The solids then flow (by gravity) down the transfer lines into receiving pots located near the grids of the two reactors. From these lower receiving pots (Figure 1-16), solids are entrained

FIGURE 1-16

PULSED SOLIDS TRANSFER POT



and transported into the reactor by timed and metered air pulses. The pulse interval, frequency and air flow rate regulate the rate at which these solids are transferred. Excess solids for discard are also removed from the regenerator by this technique.

2.7 Bed Level Control

Since the pressure drop across a fluidized bed is directly proportional to the weight of solids in that bed, the design incorporates a differential pressure transmitter circuit to measure and control the amount of material in the combustor and regenerator reactors, and therefore their bed levels at the particular fluidizing conditions. Stone transfer to control bed levels is achieved by adjustment of the on-cycle operation of the pulse feeder mixing chambers. The regenerator mixing chamber is intended to be pulsed continuously, but the chamber returning solids to the combustor will operate only when the stone inventory in the regenerator exceeds its set value. This regenerator level increase is sensed by the differential pressure cell as an increase in pressure drop across the bed, and the pulse air flow solenoid valve will open to transfer solids from regenerator to combustor.

The stone discard flow from the regenerator, and therefore the total reactor system solids inventory will be controlled similarly. Solids will be discarded from the regenerator to a water cooled receiving resevoir (Figure 1-12) when the pressure drop across the combustor bed and the pressure drop across the regenerator bed both indicate high levels. By this technique, the bed levels in both the combustor and regenerator can be controlled by automatically regulating the solids transfer and discard rates.

The regenerator receiving reservoir (Figure 1-12) will also serve to receive the solids from the regenerator cyclone. From this reservoir, the cooled solids will be transferred periodically to a second vessel (Figure 1-13) capable of being depressurized for solids removal.

2.8 Reducing Gas Generator

A reducing gas generator capable of producing 10,000 SCFH of gas at 150 psig supplies reducing gas to the regenerator. The unit is a 24 inch O.D. carbon steel cylinder internally insulated to create an 8 inch I.D. combustion chamber. The insulation is cast to form a 5 inch diameter discharge nozzle and an off-set shoulder for mating with the regenerator in such a way as to provide a means for installing a distribution plate and radiation shield.

The gas/air burner gun is AISI type 309 SS and enters via a combustion-air-cooled nozzle while the pilot enters via a 2 inch flanged nozzle on the chamber side. Two observation windows (2 inch flanged and w/ quartz windows) are provided, so oriented as to allow flame viewing, one for visual and one for infra-red scanner use. Pilot and main flame monitoring is by electronic scanner of weather-proof construction with flame detector amplifier and relay used to actuate a gas solenoid valve. A high tension electric spark for pilot ignition is provided by a 100V/10,000V transformer.

2.9 Supporting Structure

Figure 1-17 shows the supporting structure designed for the FBCR Miniplant. Overall, this structure stands 34 feet tall, is 20 feet wide and 10.5 feet deep and is constructed of 8 inch wide flange steel beams. Three platform levels at 8, 16 and 24 feet are provided for servicing the unit and are reached by a stairway attached to the outside of the frame. A five ton bridge hoist at the top unit is provided for assembling and disassembling the unit.

FIGURE 1-17

SUPPORTING STRUCTURE

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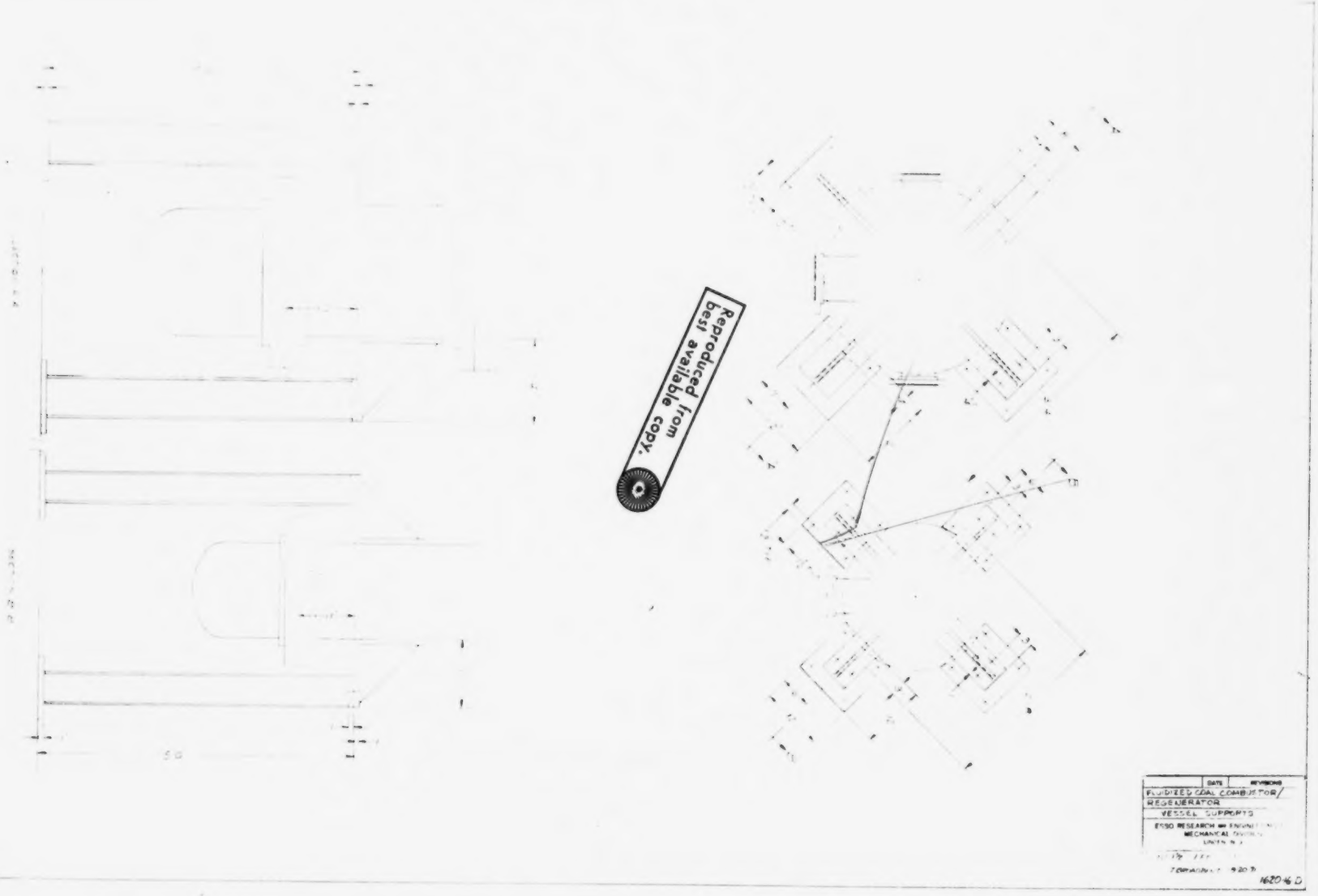
FIGURE 1-18

VESSEL SUPPORT LEGS



The combustor and regenerator reactors are each supported on four legs connected to the reactors by reinforcing gussets above the grids (see Figure 1-18). The steel structure contains guides at 8 foot intervals to accommodate thermal expansion of the reactor in the vertical direction.

2.10 Miscellaneous Equipment

- An auxillary compressor with a capacity of approximately 200 SCFH at 175 psig is intended to supply air necessary for the pulse feeders, purge lines, combustor start-up burner and internal fluidizing lines. The higher pressure is necessary to assure flow of this special purpose air into the reactors.
- A gas burner exhausting into the fluidized bed combustor is provided for unit start-up at atmospheric pressure. Fuel for this burner and for the reducing gas generator is supplied through metering controls from a 300 gallon LNG storage tank.
- The system has been designed to allow effluent gasses from the combustor and regenerator to be combined and passed through a particulate filter and/or scrubber for fly ash, lime and SO_2 removal before discharge to the atmosphere.
- Pressure, temperature and gas sampling taps are provided at many locations in the combustor.

3. DESIGN VERIFICATION WITH THE COLD MODEL TEST UNIT

For the purpose of verifying the design of the pulsed air solids transfer system used in the design of the FBCR Miniplant, and to permit visual observation of its fluidization characteristics, a Cold Model Test Unit (CMTU) was built. The CMTU is a two vessel fluidized solids system constructed from Plexiglass, a transparent acrylic plastic. The CMTU was designed to operate at ambient temperature and pressures up to 60 psig.

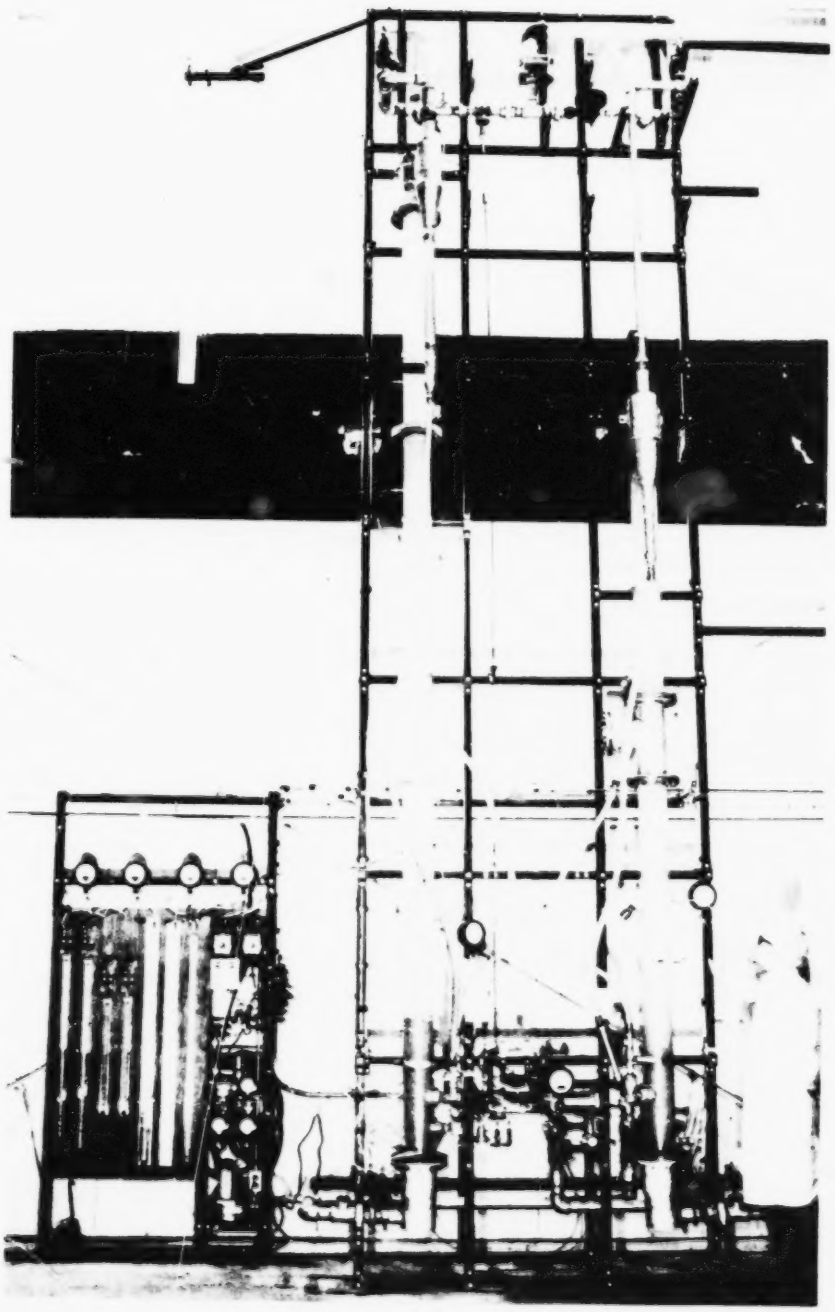
3.1 Features of the CMTU

Figure 1-19 is a picture of the CMTU. The unit consists of two 5.5 inch I.D. vessels simulating the combustor and regenerator of the FBCR Miniplant. The simulated combustor (i.e., the vessel on the left in Figure 1-19) is 18 feet tall and was assembled from 3 flanged sections. The regenerator is made of 2 flanged sections and stands 12 feet tall. Both vessels have bottom plenum chambers and grids for distributing the fluidizing air and single stage aluminum cyclones for removing entrained solids. These solids can be returned to the fluidized beds or collected as desired.

One inch I.D. nylon reinforced transparent PVC hose is used for solids transfer between the two vessels. This permits visual observation of solids movement in these lines which connect the upper part of the vessel transferring the solids to the lower part of the vessel receiving them. The small receiving-injection pots to which the bottom of these lines are attached are equipped with fluidizing and pulsed air. In some of the solids transfer studies, the use of an overflow collector was

FIGURE 1-19

THE COLD MODEL TEST UNIT



investigated as a means of creating an enlarged solids reservoir in the transmitting vessel. In the FBCR Miniplant, such a reservoir would serve to insure a continued solids seal in the transfer legs and minimize back-flow of gases between reactors. The enlarged reservoir, shown on the regenerator vessel in Figure 1-20, was constructed of a 6 inch I.D. aluminum tee with a plate on the inside to serve as a solids baffle and a plexiglass window on the outside for observation of the solids.

In addition to studying solids transfer techniques, the CMTU was used to determine what effect the hair pin heat transfer loops designed for the FBCR Miniplant would have on the fluidization characteristics of the combustor. Figure 1-21 shows a simulated heat transfer loop section that was used in the CMTU. It was fabricated of 3/8 inch aluminum as a prototype half-scale version with the same configuration and pitch as the FBCR Miniplant design.

Gas flow rates to each of the two reactors of the CMTU could be varied. A control panel situated to the left of the plexiglass vessels permitted measurement of their flow rates and of their individual bed pressure drops. It also controlled and measured the pressure differential between beds, and provided a means of varying the on-off pulsing times and the air flow rates for the solids transfer pots.

3.2 Solids Transfer Studies

The pulsed gas-solids transfer technique that was selected for the design of the FBCR Miniplant has been used successfully at the Esso Research Center in England (3) for transferring solids between the two atmospheric pressure chambers of its continuous CAFB pilot unit. The

use of this technique in pressurized systems had not been demonstrated however, prior to the CMTU studies. Based on the results obtained in the CMTU studies, it is now clear that:

1. Solids can be transferred between fluidized bed reactors under pressure at a controlled and adjustable rate using the pulsed-air technique. This has been verified at pressures up to 40 psig and fluidizing velocities up to 10 fps.
2. The solids transfer rate can be controlled by changing the on-off pulse cycle time or the pulse air flow rate.
3. The bed level control system designed for the FBCR Mini-plant works. This technique, which consists of continuously pulsing one of the transfer receiving pots and controlling when the other is pulsed by the pressure differential between beds, is able to maintain constant bed levels in both vessels of the CMTU without any adjustment to the controls once they were set.
4. The use of a solids reservoir decreases the likelihood of inadvertently emptying the transfer legs completely of solids.
5. An increase in system pressure decreases the solids transfer rate that can be achieved with a given pulse cycle time and gas flow rate.
6. Solids ranging in their properties from glass beads (7 to 10 mesh and 110 lbs/ft^3 bulk density) to limestone (-6 mesh and 85 lbs/ft^3 bulk density) can be transferred using the pulsed gas technique.

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FIGURE 1-20

SOLIDS TRANSFER RESERVOIR

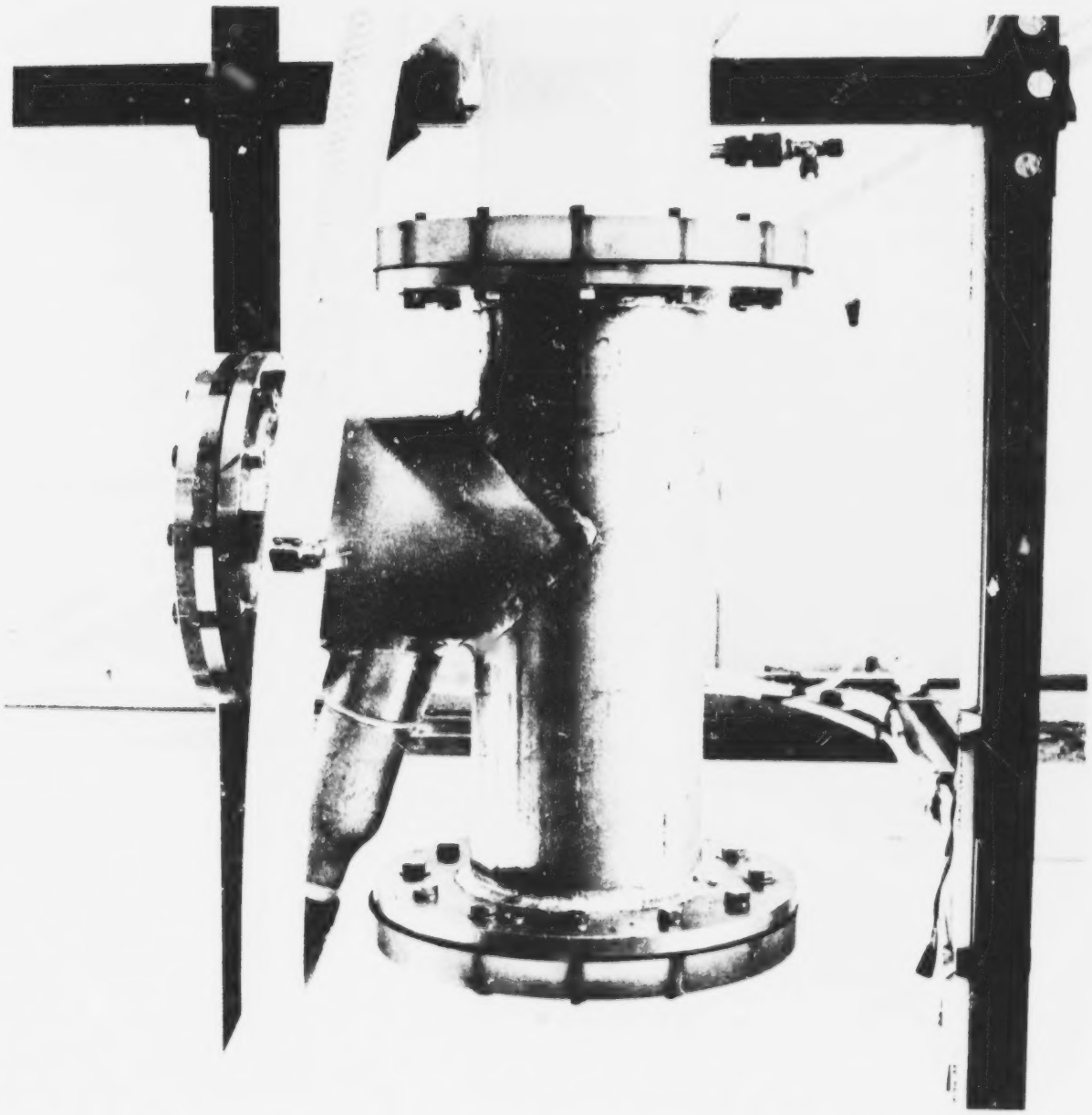

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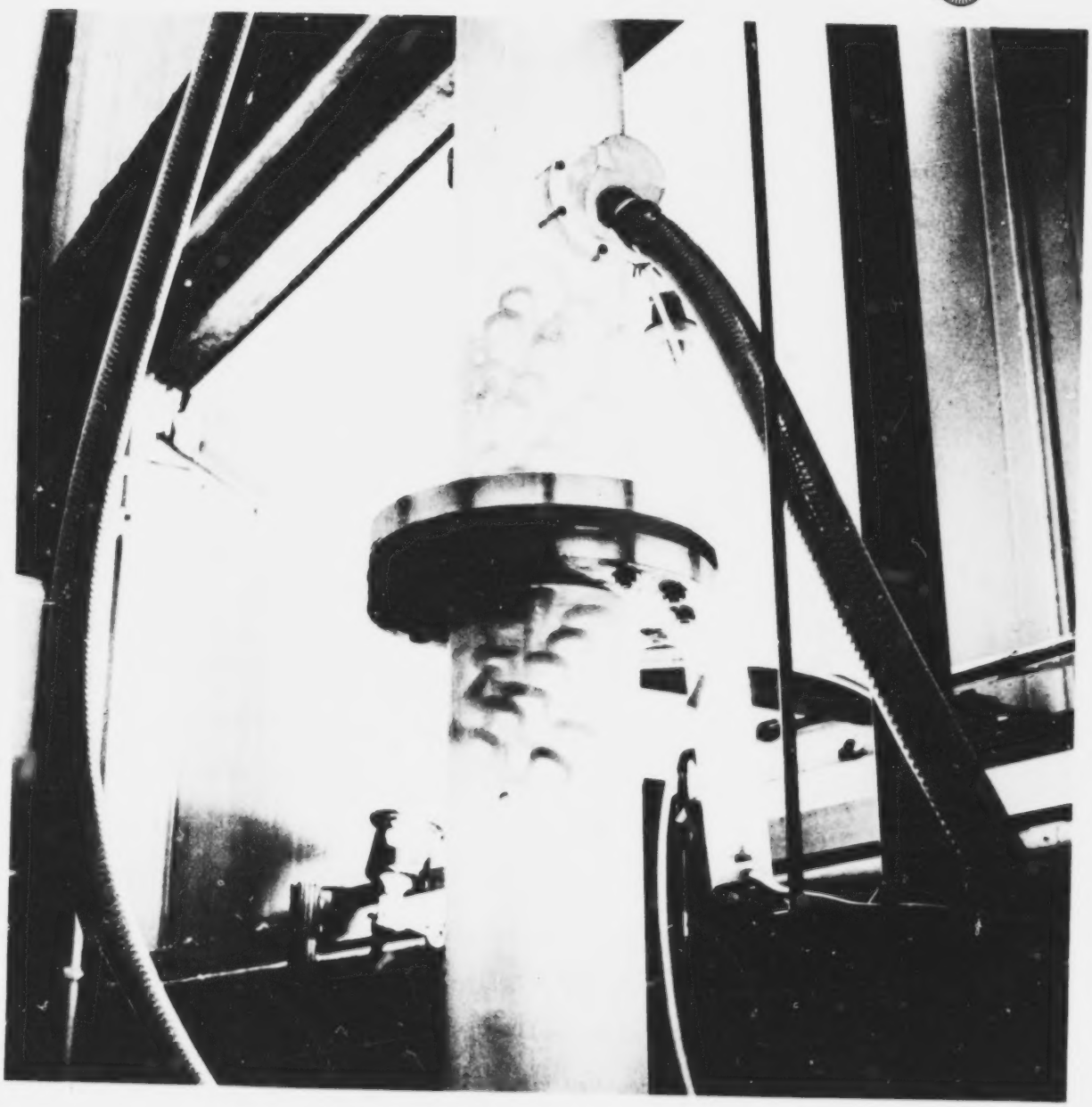
FIGURE 1-21

SIMULATED HEAT TRANSFER LOOP



3.3 Solids Fluidization and Entrainment

3.3.1 Predicted Regenerator Bed Slugging Height

The fluidization and entrainment characteristics to be expected in the regenerator of the FBCR Miniplant were studied in the CMTU. The taller of the two CMTU vessels was used in these studies but without the simulated heat transfer section. The range of parameters investigated is shown in Table 1-2.

Table 1-2

Parameters in CMTU Entrainment and Fluidization Studies

Superficial Gas Velocity, ft/sec	4, 6, 8 & 10
Settled Bed Height, ft	2 & 3
Vessel Pressure, psia	15, 40 & 60
Fluidized solids	7 to 10 mesh glass beads & -6 mesh limestone

In the way of qualitative observations, slugging of the bed was found to be worse with the spherical glass beads than with the wide cut limestone. The quality of the fluidization also deteriorated with increasing settled bed depth, more so for the limestone than for the glass beads. At a settled bed height of 3 feet, the slugging behavior of the limestone and glass beads became similar. When the maximum slugging height exceeded the vessel outage and slugs of solid particles entered the cyclone, bridging of the cyclone solids outlet tube would occur resulting in a total loss of solids capture capability.

Figures 1-22 and 1-23 show the mean and maximum bed heights obtained in the CMTU with the -6 mesh limestone material as a function of gas velocity, settled bed height, and operating pressure. The particle size distribution for the limestone is shown in Figure 1-24.

Using the data shown in Figure 1-22, equation (1-1) for predicting the average slug height was derived using a least squares regression technique.

$$H_{\bar{s}} = 0.265\ h^{0.5}\ p^{0.4}\ (U-v.)^{0.82} \qquad (1\text{-}1)$$

$H_{\bar{s}}$ = average slug height above the settled bed in feet

h = settled bed height in feet

p = fluidizing gas pressure in psia

U = superficial gas velocity in ft/sec

v = incipient fluidization velocity in ft/sec

Since the regenerator diameter in the FBCR Minipiant design approximates that in the CMTU, equation (1-1) can be used directly to approximate the regenerator height that will be required for the continuous pilot unit. Considering the maximum operating conditions for which the FBCR Miniplant has been designed (see Table 1-1) and assuming a settled bed height of 3 feet, equation (1-1) predicts an average slug height of 11 feet for the regenerator. As shown in Figure 1-23, the maximum slug height will be about 3 to 4 feet higher than this. Thus, the FBCR Miniplant design which calls for an overall regenerator height of about 16 feet from the grid to the outlet should

satisfy the most extreme slugging conditions expected in the pilot unit. If this turns out not to be the case, a baffle could be easily installed in the regenerator prior to the cyclone to break-up the slugs of solids.

3.2.2 Predicted Combustor Bed Slugging Height

The use of equation (1-1) for determining the slugging height in the 12.5 inch combustor designed for the FBCR Miniplant should result in too high a predicted value. This is so because its larger diameter, and the baffling provided by its heat transfer loops, should make this reactor much less conducive to solids slugging than is the regenerator. At the extreme operating conditions for which the FBCR Miniplant has been designed (see Table 1-1), and a settled bed height of 2 feet, this correlation predicts a mean slug height of about 17 feet. Thus, the maximum slug height obtained in the combustor should be well within the 23 feet provided by the pilot plant design.

FIGURE 1-22

MEAN SLUG HEIGHT OBSERVED IN CMTU STUDIES

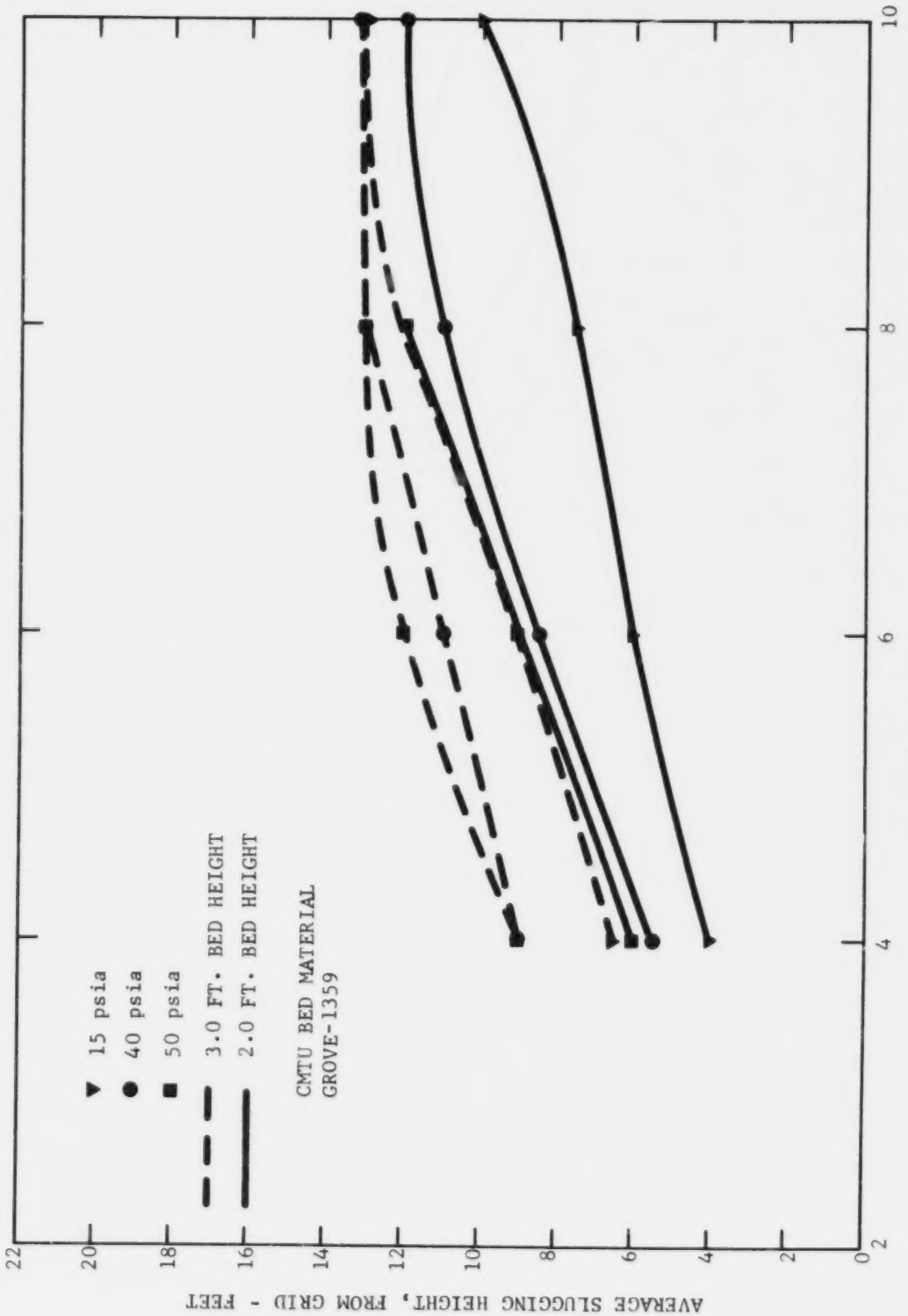


FIGURE 1-23

MAXIMUM SLUG HEIGHT OBSERVED IN CMTU STUDIES

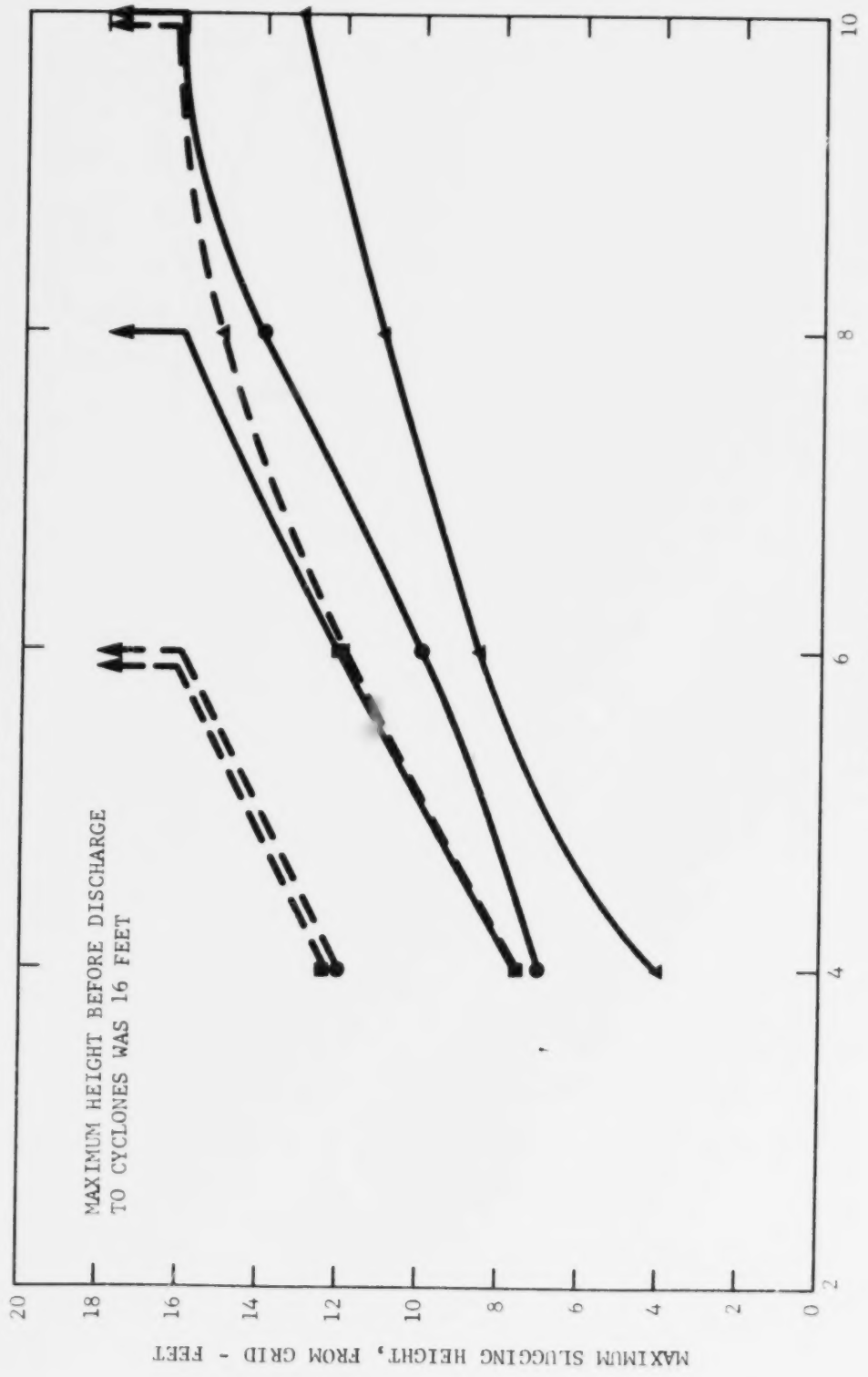
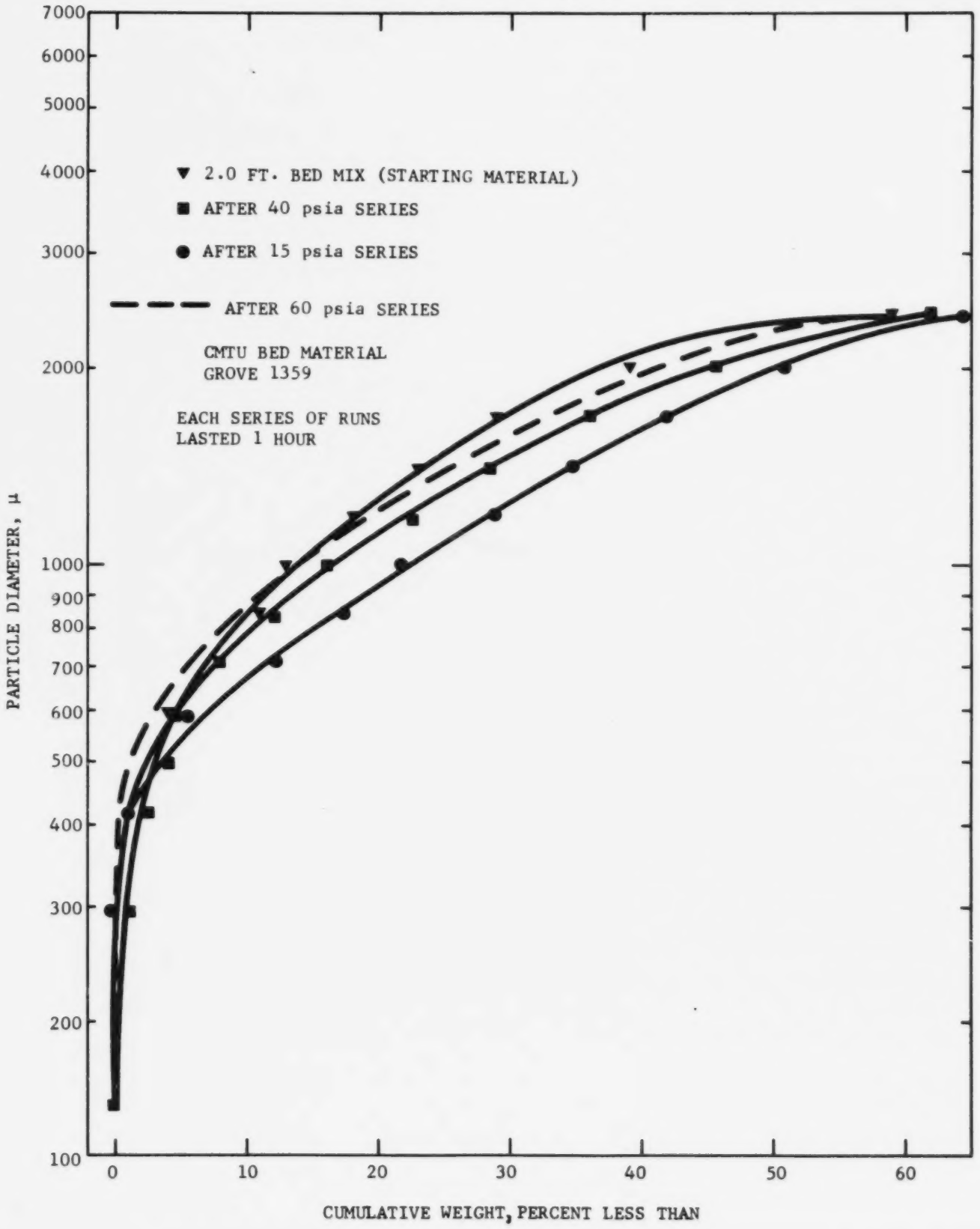


FIGURE 1-24

PARTICLE SIZE DISTRIBUTION OF BED MATERIAL USED IN CMTU STUDIES



PART II

FACTORS AFFECTING NO_x FORMATION AND CONTROL IN FLUIDIZED BED COMBUSTION

Part II of this report deals with the experimental study of NO_x formation and control in fluidized bed combustion that was carried out as part of Contract CPA 70-90 for EPA's Office of Air Programs. The experimental equipment and procedures used in this study, data obtained, and the analyses of the results are presented in the following sections.

1. EXPERIMENTAL APPARATUS, MATERIALS AND PROCEDURES

The experimental equipment used for this study of NO_x formation and control consisted of a fluidized bed coal combustion unit and two fixed bed reaction units.

1.1 Fluidized Bed Coal Combustion Unit

A schematic diagram of the Esso fluid bed combustion unit is shown in Figure 2-1. The three primary components of this unit were: (1) the coal feeding system, (2) the fluidized bed reactor, and (3) the gas cleanup and analysis system.

1.1.1 Coal Feeding Equipment

Coal was stored in a small hopper and gravity-fed to a vibrating low rate solids Vibro-Feeder. The output of the feeder was connected by pneumatic tubing to a 1/4 inch stainless steel tube, extending through the reactor grid approximately 1/8 inch into the bed. A small baffle was located directly above the coal inlet to promote dispersion. The feed rate of the coal was controlled by adjusting the vibration intensity of the feeder.

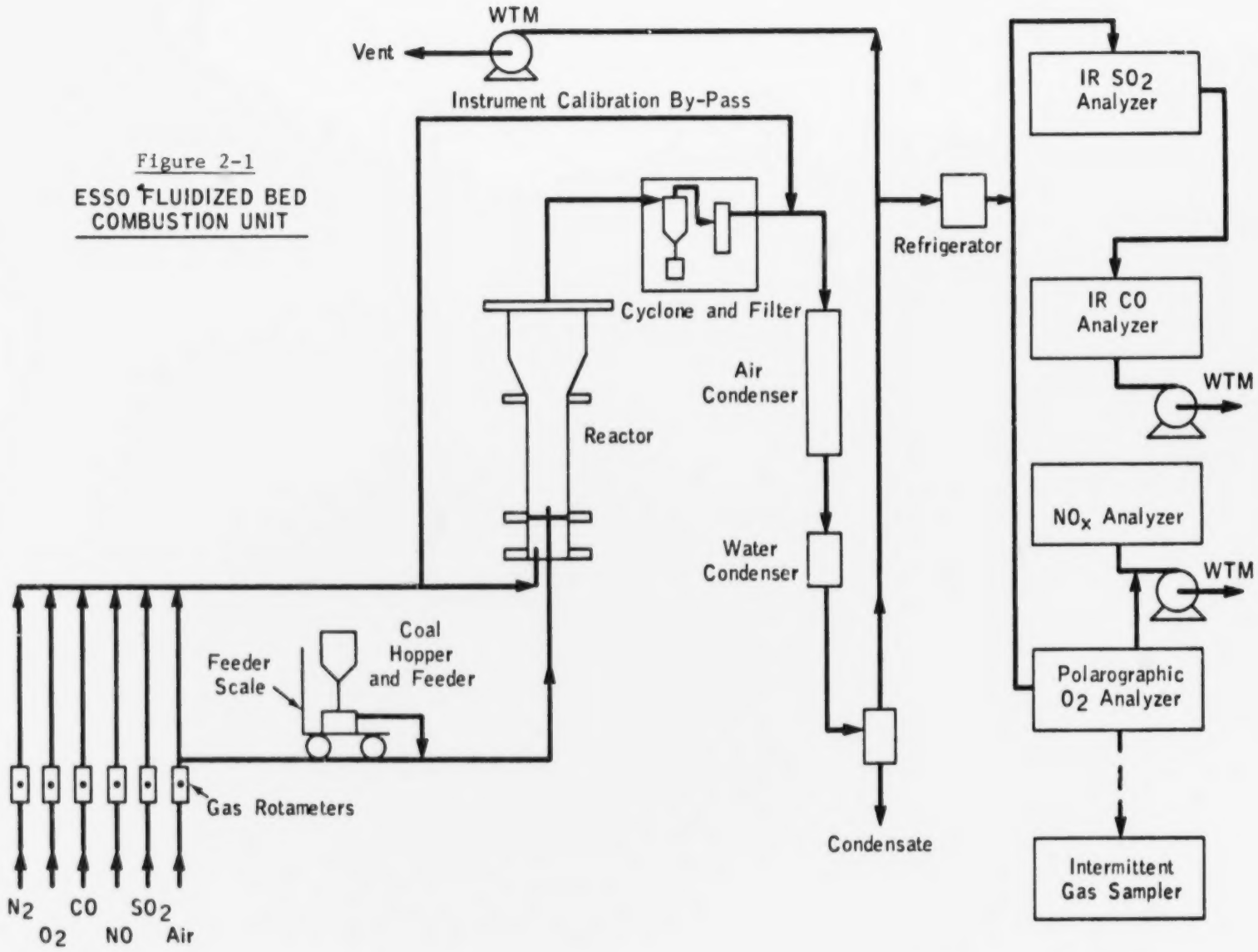
1.1.2 Fluidized Bed Reactor

A schematic diagram of the fluidized bed reactor used as the coal combustor in this study is shown in Figure 2-2. This reactor consisted of an air preheat section, a reactor section, and a disengaging section. The entire reactor was constructed of an Incoloy 800 alloy.

The air preheat section was a three inch diameter, eight inch high section, packed with 1/4 inch ceramic cylinders. It was attached directly to the reactor section. Beaded electrical heaters supplied the necessary heat to preheat the air to 600°F. The air preheat temperature was automatically controlled at the desired level.

Figure 2-1

ESSO FLUIDIZED BED COMBUSTION UNIT



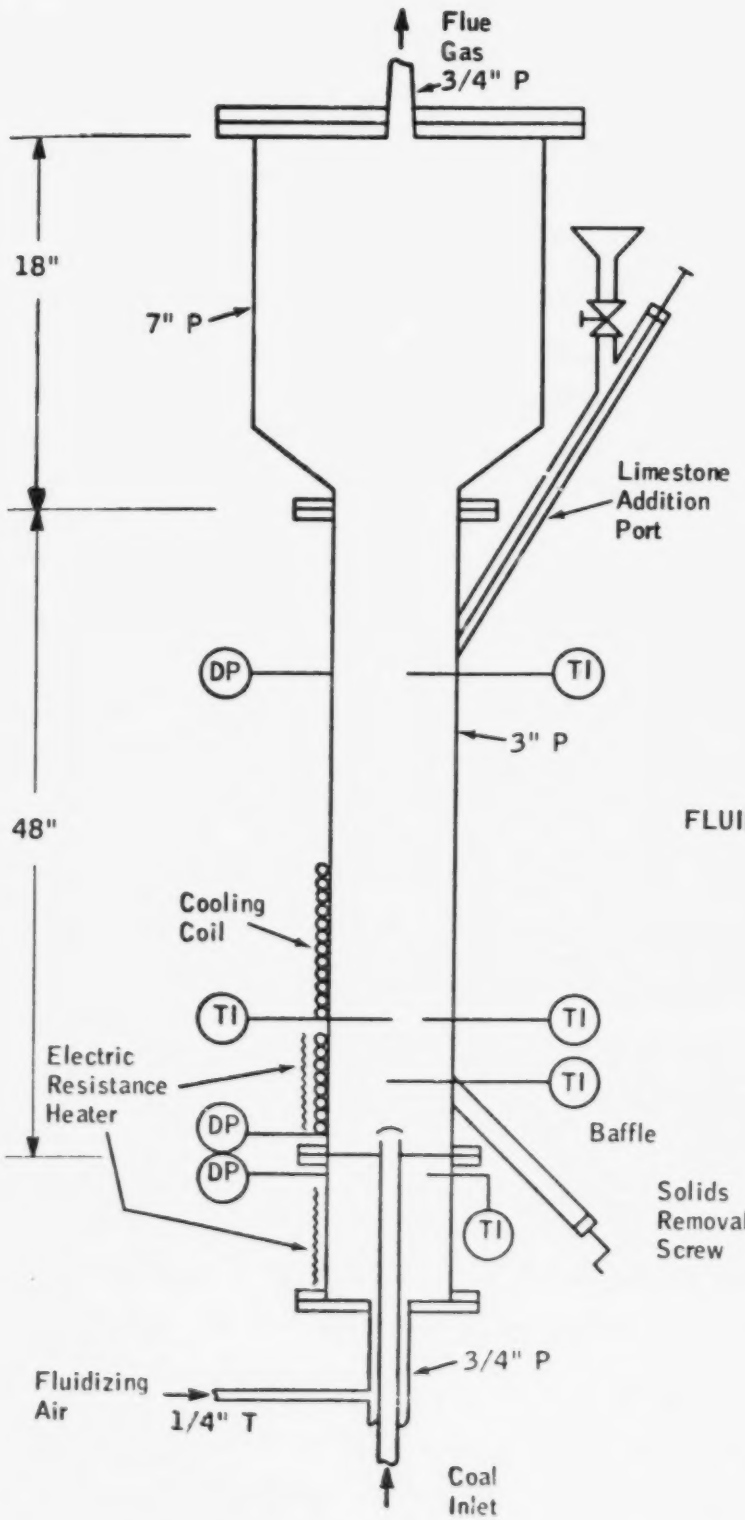


Figure 2-2

FLUIDIZED BED COMBUSTOR

The reactor was a three inch diameter, four feet high Incoloy tube. Air distribution was accomplished by six bubble caps, with eight 5/64 inch outlet holes in each bubble cap. The bed was preheated by use of beaded, resistance wire heaters. Bed temperature was controlled by use of an external cooling water coil. The water flow rate to the cooling coil was manually adjusted to yield the desired temperature. The bed was insulated to limit heat loss to the atmosphere. Average bed temperature was determined by five thermocouples in the bed. Pressure drop across the bed was continuously determined by use of a water manometer. Withdrawal of bed solids was accomplished by use of a screw conveyor and fresh limestone was batch charged to the unit by use of the inlet port located three feet above the distributor plate.

The disengaging section was a seven inch diameter, 18 inch high section, in which the gas velocity was reduced to allow some entrained particles to be returned to the bed.

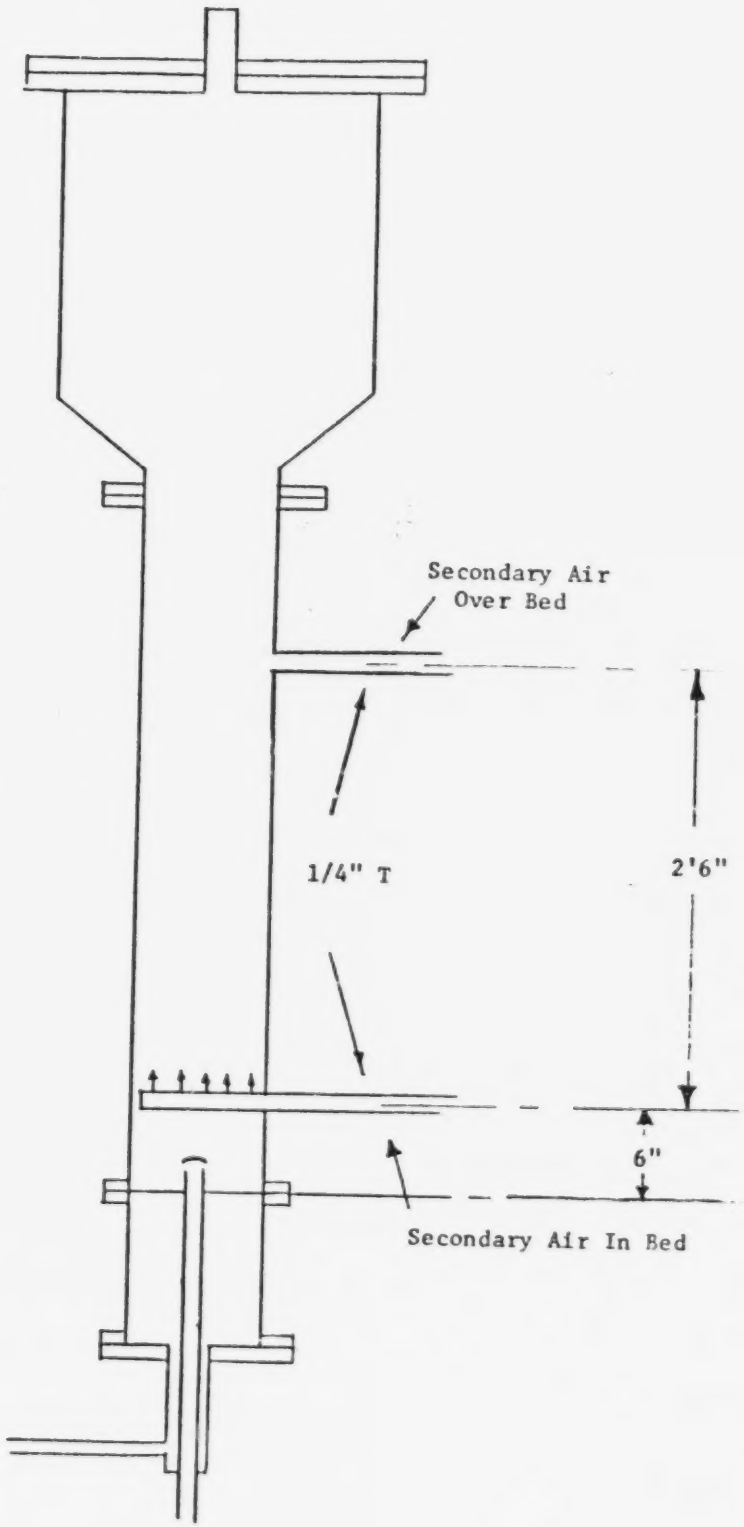
During the course of the study on nitrogen oxides, the fluidized bed reactor was modified to permit staged air addition to the combustor. This modification, shown in Figure 2-3, consisted of adding secondary air ports at 0.5 and 2.5 feet above the primary air distributor grid. The purpose of this modification was to study the effect of staged combustion on NO_x emissions.

1.1.3 Gas Cleanup and Analysis System

The gas cleanup and analysis system that was used is also shown in Figure 2-1. The gas exited the reactor through a 3/4 inch uninsulated pipe. The temperature of the gas dropped to approximately 300°F before entering a glass cyclone and a fritted stainless steel filter. The gas leaving the filter was essentially free of entrained particulates.

FIGURE 2-3

STAGED COMBUSTION REACTOR



The cyclone and filter were enclosed in an electrical oven to prevent any moisture condensation.

The particulate-free flue gas was then passed through an air-cooled condenser and a water-cooled condenser to remove most of the water vapor. Approximately 50 percent of the flue gas was then metered by a large wet test meter and vented; the remaining flue gas (0.5 CFM) was diverted through a refrigerator which lowered the dew point of the gas to 35°F before it was sent to the gas analysis equipment. The gas analysis equipment included: Beckman Model NDIR315 Analyzers for SO_2 and CO, a Beckman Model 715 polaragraphic analyzer for O_2, and a Whittaker polaragraphic NO_x analyzer. During the program, a Dupont Model 461 NO_x analyzer and a Beckman Model NDIR315B NO analyzer were also used. The Dupont analyzer measures both NO and NO_2. NO_2 is measured directly by absorption of visible light while the NO is measured by oxidizing the sample gas to NO_2 under 60 psia oxygen pressure and measuring the resulting NO_2 concentration. A single determination of both NO and NO_2 typically required five minutes with the Dupont analyzer.

1.2 Fixed Bed Reactors

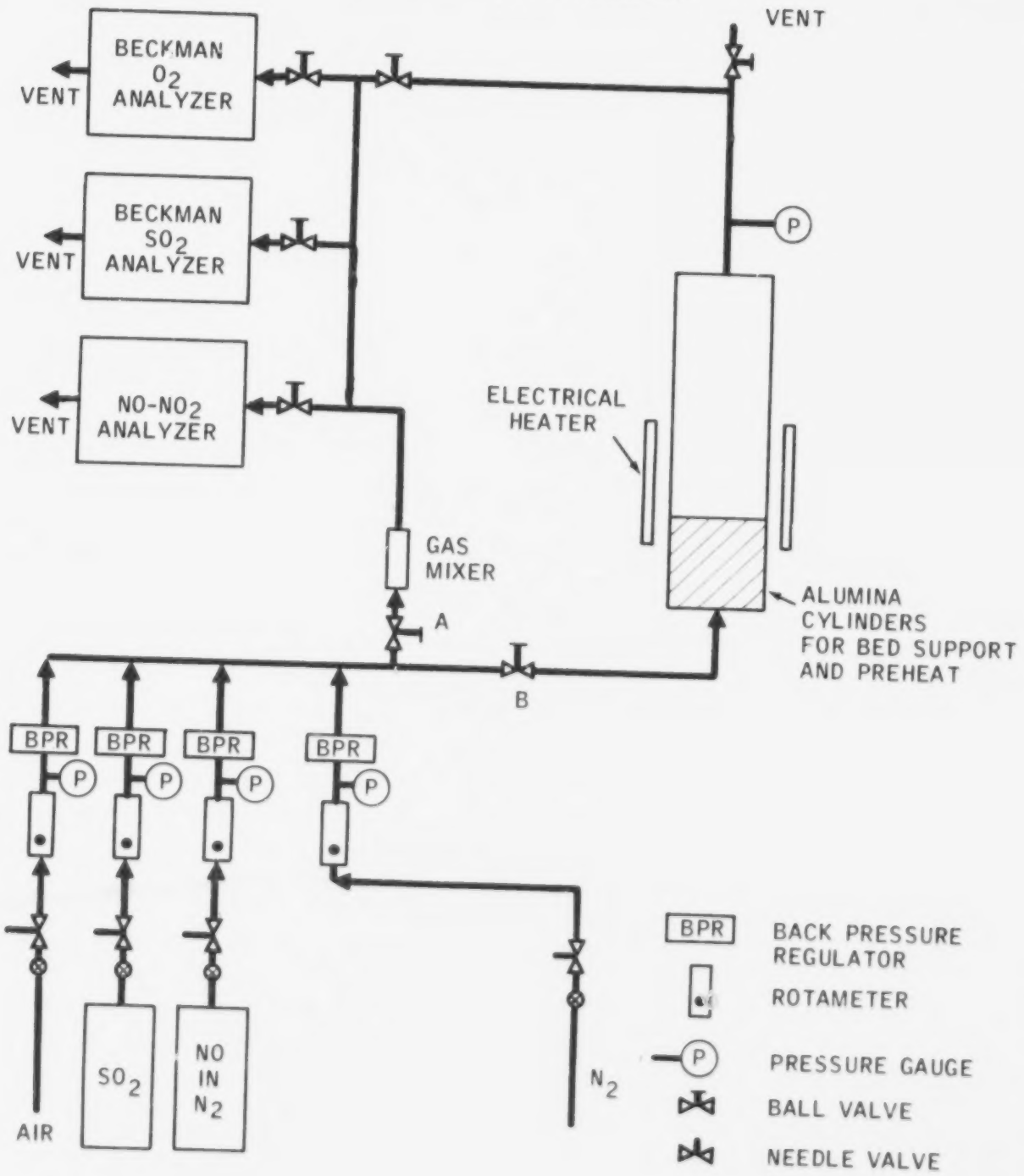
1.2.1 2.5 Inch Reactor System

A schematic diagram of the basic fixed bed reactor system used in this study is shown in Figure 2-4. This system was equipped to operate with either upward or downward flow of gas. Cylinder gases of NO, SO_2 and CO were used to investigate possible reaction systems occurring in the Esso FBC. Inlet and outlet NO, SO_2, O_2 and CO concentrations were measured using the instrumentation described in Section 1.1.3. Most of the studies made with this system were carried out in a 2.5 inch O.D. (2.25 inch I.D.) ceramic tube externally heated by an electric furnace.

Figure 2-4

FIXED BED REACTOR

(Shown for Upflow Operation)



1.2.2 1 Inch Reactor System

In addition to the 2.5 inch ceramic reactor, a 1 inch O.D. stainless steel reactor (3/4 inch I.D.) was used to carry out fixed bed reaction experiments on an even smaller scale. The same gas blending and analysis equipment was used with this reactor as was used with the 2.5 inch reactor.

1.3 Feed Materials

1.3.1 Limestone

The limestone that was used in this study was obtained from the Grove Lime Company, Stephen City, Virginia. The chemical analysis of this stone is shown in Table 2-1, and the various particle size distributions used are given in Figure 2-5. Calcined stone was used primarily, but not exclusively, in this study. The normal calcining procedure and conditions are given in Appendix 2.

The bulk and particle densities of the stone are given in Appendix 3A, along with the experimentally determined minimum fluidizing velocity curves.

Table 2-1

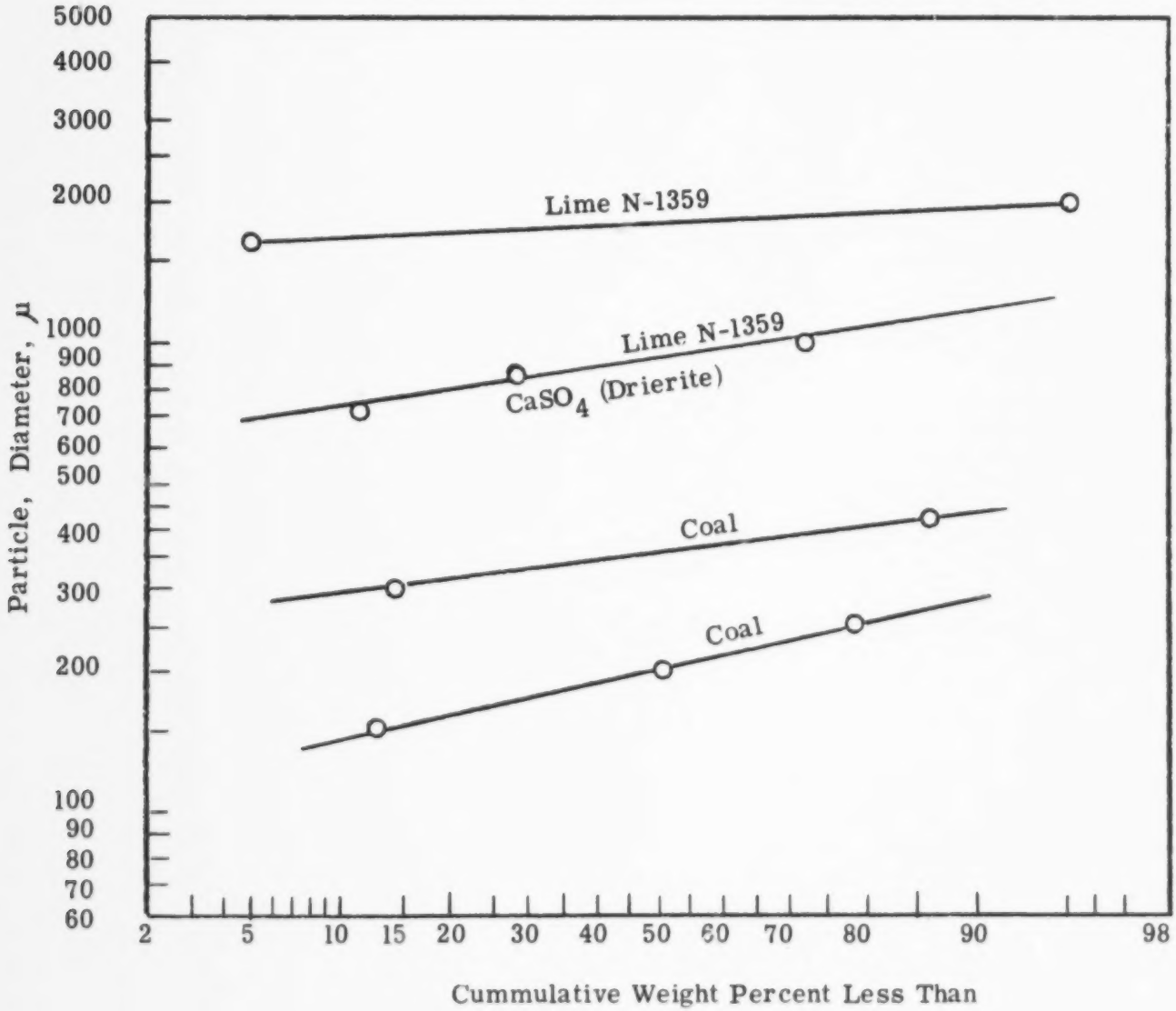
Composition of Limestone
Used in Esso FBC Program

Limestone - Grove N -1359

Component	Wt Percent
CaO	97
MgO	1.16
SiO_2	1.07
Al_2O_3	0.29

Figure 2-5

PARTICLE SIZE DISTRIBUTIONS OF LIMESTONE AND COAL FEEDS TO ESSO FBC



1.3.2 Coal

The coal used was a high-volatile (A) bituminous coal from Northern West Virginia. It was obtained from the Humphrey Preparation Plant, Christopher Coal Company, a division of Consolidation Coal Company, Inc. The Bureau of Mines at Morgantown, West Virginia, obtained the coal from the preparation plant and subsequently shipped it to Esso. The chemical analysis of this coal is given in Table 2-2. The particle size analysis of the coal is given in Figure 2-5.

Table 2-2

Composition of Coal
Used in Esso FBC Program

Coal - Pittsburgh Bituminous (A)

Proximate Analysis		Ultimate Analysis	
Component	Wt. Percent	Component	Wt. Percent
Moisture	1.2	Ash	9.0
Volatile Matter	6.5	H	5.3
Fixed Carbon	53.3	C	74.1
Ash	9.0	N	1.4
		S	3.0
		O (by diff.)	7.3

1.3.3 Alundum and $CaSO_4$

Abrasive-grade Alundum (20 mesh) was used as a bed material in selected runs. (The minimum fluidizing velocity and the bulk density of this material are given in Appendix 3B.)

$CaSO_4$ (Drierite) was also used as a bed material. (The minimum fluidizing velocity and bulk density of the $CaSO_4$ also are given in Appendix 3B.) The particle size distribution of $CaSO_4$ was the same as the particle size distribution of the smaller lime, as shown in Figure 2-5.

1.4 Experimental Procedures

1.4.1 Fluidized Bed Combustor

The startup of the Esso FBC was accomplished by batch addition of the desired amount of bed material to the unit and preheating the bed to approximately 1200°F. Upon reaching this temperature, coal feed to the unit was initiated. When the desired operating temperature of the unit was approached, the coal feed rate was adjusted to the desired operating rate and cooling water was introduced to the cooling coil for control of the bed temperature. A steady combustion condition was assumed to be achieved when both the bed temperature and O_2 level in the flue gas stabilized.

Samples of the cyclone solids and bed solids were taken intermittently as the run progressed. At the termination of a run, samples of the bed and cyclone solids were also obtained. These solid samples were analyzed for carbon, sulfate, and sulfur, as desired.

1.4.2 Fixed Bed Reactors

The experimental procedure followed in using either one of the fixed bed reactors was as follows:

1. The reactor would be charged with the desired bed material and electrically heated to the desired temperature. Nitrogen and argon would be used as purge gases during the heatup period.
2. The inlet composition of the reactant gases (blended mixtures of NO, SO_2 and CO) would be determined.
3. The reactant gases would then be fed to the fixed bed reactor (either upflow or downflow), and the outlet gas compositions continuously monitored.

2. GENERAL CONSIDERATIONS OF NO_x FORMATION AND CONTROL IN FLUIDIZED BED COAL COMBUSTION

The oxides of nitrogen, NO and NO_2 (collectively referred to as NO_x), can be formed in a combustion process by the direct combustion of atmospheric nitrogen and oxygen as given by equation (2-1). As shown

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (2\text{-}1)$$

in Figure 2-6, the equilibrium NO concentration in this system is low, less than 100 ppm, at commonly employed temperatures in fluidized bed combustion of 1500 to 1700°F. Hence, it was originally anticipated that NO emissions from fluidized bed combustion systems would be low.

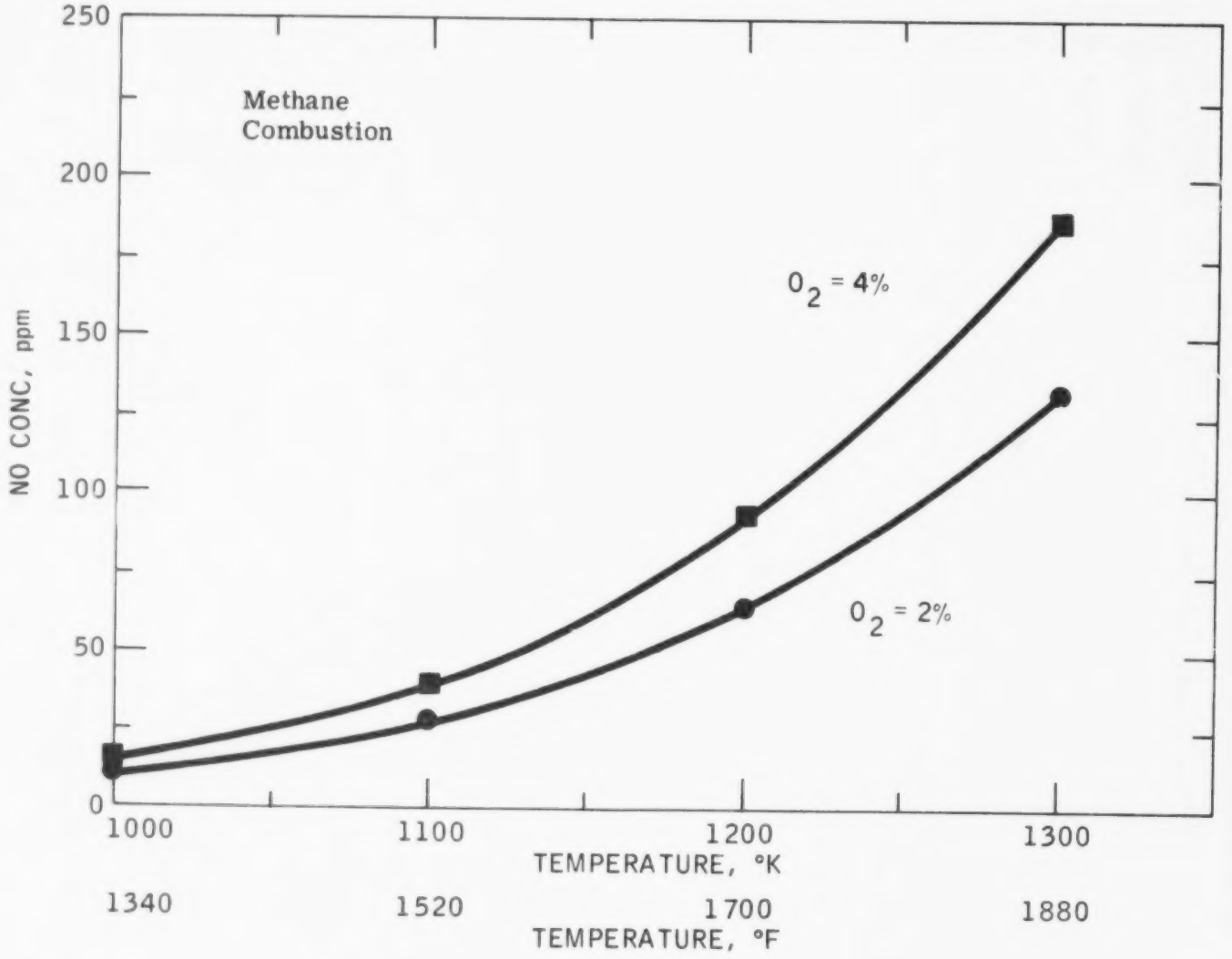
Experimental studies at Esso have shown, however, that NO emissions greater than 1000 ppm can be obtained in a fluidized bed combustor operating at 1600°F. Such concentrations are considerably above the equilibrium concentration for NO shown in Figure 2-6 at a temperature of 1600°F. Research conducted at Argonne National Laboratories (4) has shown that the oxidation of fuel nitrogen is the primary mechanism for NO formation in fluidized bed combustion. This oxidation can be conceptually represented by equation (2-2).

$$N_{fuel} + 1/2\ O_2 \longrightarrow NO \qquad (2\text{-}2)$$

The rate of reaction (2-2) is very fast compared to the rate for the reverse reaction (2-1) and it is conceivable that all of the fuel nitrogen is initially converted to NO. The concentration of NO appearing in the flue gas would then be dependent upon subsequent reaction of the

Figure 2-6

THERMODYNAMIC EQUILIBRIUM NO CONCENTRATION



NO in the bed. Prior to the studies described in this report, the following observations had been made by various investigators concerning NO emissions from fluidized bed combustors:

1. The NO emissions from the FBC with a partially-sulfated lime bed are 20 to 40 percent lower than the emissions (under similar operating conditions) using an inert bed. (4)
2. The addition of Co_3O_4 to a FBC, operating with an inert bed material, causes an increase in NO emissions, indicating that Co_3O_4 may have an accelerating effect on the oxidation of fuel nitrogen (4).
3. The NO emissions from a FBC with a lime bed (zero sulfation) are higher than corresponding emissions with an inert bed. These higher emissions may reflect a catalytic effect of the lime on the rate of oxidation of fuel nitrogen (1).
4. NO and SO_2 react over a partially sulfated lime bed to yield lower NO emissions. No reaction occurs over an inert bed or $CaSO_4$ (1).

These results served as the starting point for the basic and applied studies described in Section 3 of this part of the report.

3. EXPERIMENTAL RESULTS

3.1 Effect of Bed Temperature and Excess Air on NO_x Emissions

NO_x emissions resulting from the reaction of atmospheric nitrogen and oxygen in conventional combustion equipment are known to be very much influenced by the oxygen concentration of the flue gas (i.e., the excess combustion air level) and the temperature in the combustion zone. On the other hand, in fluidized bed combustion where most of the NO_x is formed by oxidation of the organic nitrogen in the coal, detailed studies have not been made to define the effect of excess air level and bed temperature on the conversion of the fuel nitrogen to NO_x. The initial series of FBC experiments were designed therefore to obtain such data. Alundum (Alumina) and Drierite ($CaSO_4$) were used as the fluidized bed materials in these experiments since these materials, unlike lime or limestone, would be inert to reaction with SO_2 formed from the oxidation of the sulfur in the coal. Consequently, the SO_2 concentration would remain constant and would not be an influential variable in these studies. This was essential since it had been shown in previous work at Esso Research (1) that SO_2 and NO reacted in the presence of lime at fluidized bed combustion conditions.

The use of Alundum as a bed material provided a base condition to which emissions with lime and $CaSO_4$ could be compared. $CaSO_4$ was used since it is the product formed when lime is used as the fluidized bed medium for SO_2 emissions control. Therefore, any catalytic effect that the formation of $CaSO_4$ would have on NO emissions would be maximized by its use as the bed material.

Figure 2-7 shows the NO emissions obtained operating the fluidized bed combustor with the lime, alundum and $CaSO_4$ bed materials. The NO_2 emissions were essentially zero in these tests, and for that matter, in all subsequent fluidized bed combustion tests that were carried out. The NO emissions using $CaSO_4$ were constant at 615 ppm. With the Alundum bed, the NO emissions were higher at 725 ppm, but still constant. The SO_2 emissions in both these test were constant at a level of about 2500 ppm, corresponding to complete conversion of the fuel sulfur to SO_2. Initial NO emissions with the lime bed were the highest observed at about 920 ppm. As the run progressed, however, these emissions appeared to asymptote to about the same NO level obtained using the $CaSO_4$ bed.

3.1.1 Bed Temperature

The NO emissions from the Esso FBC were monitored over the range of bed temperatures from 1400°F to 1800°F with Alundum and $CaSO_4$ as the bed materials. Complete data reduction for these runs is given in Appendix 4. The NO emissions are shown in Figure 2-8, as function of bed temperature, for these two bed materials. The NO emissions using the Alundum bed, were consistently higher than the corresponding emissions with the $CaSO_4$ bed, indicating that some sort of catalytic reduction (or reaction) of NO was occurring over $CaSO_4$. Interestingly, the difference between the NO emissions obtained with the Alundum and $CaSO_4$ beds increased as bed temperature was decreased. This result indicates that whatever phenomenon was acting to reduce NO emissions over the $CaSO_4$ bed was being accelerated at low bed temperatures.

FIGURE 2-7

NO EMISSIONS USING DIFFERENT BED MATERIALS

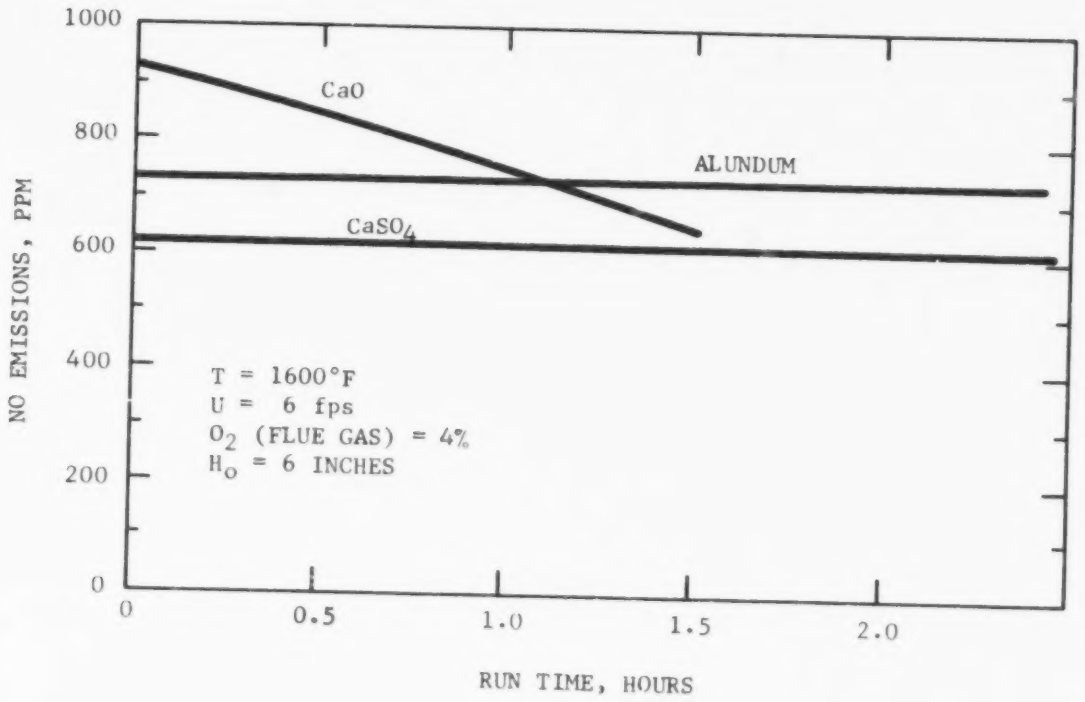
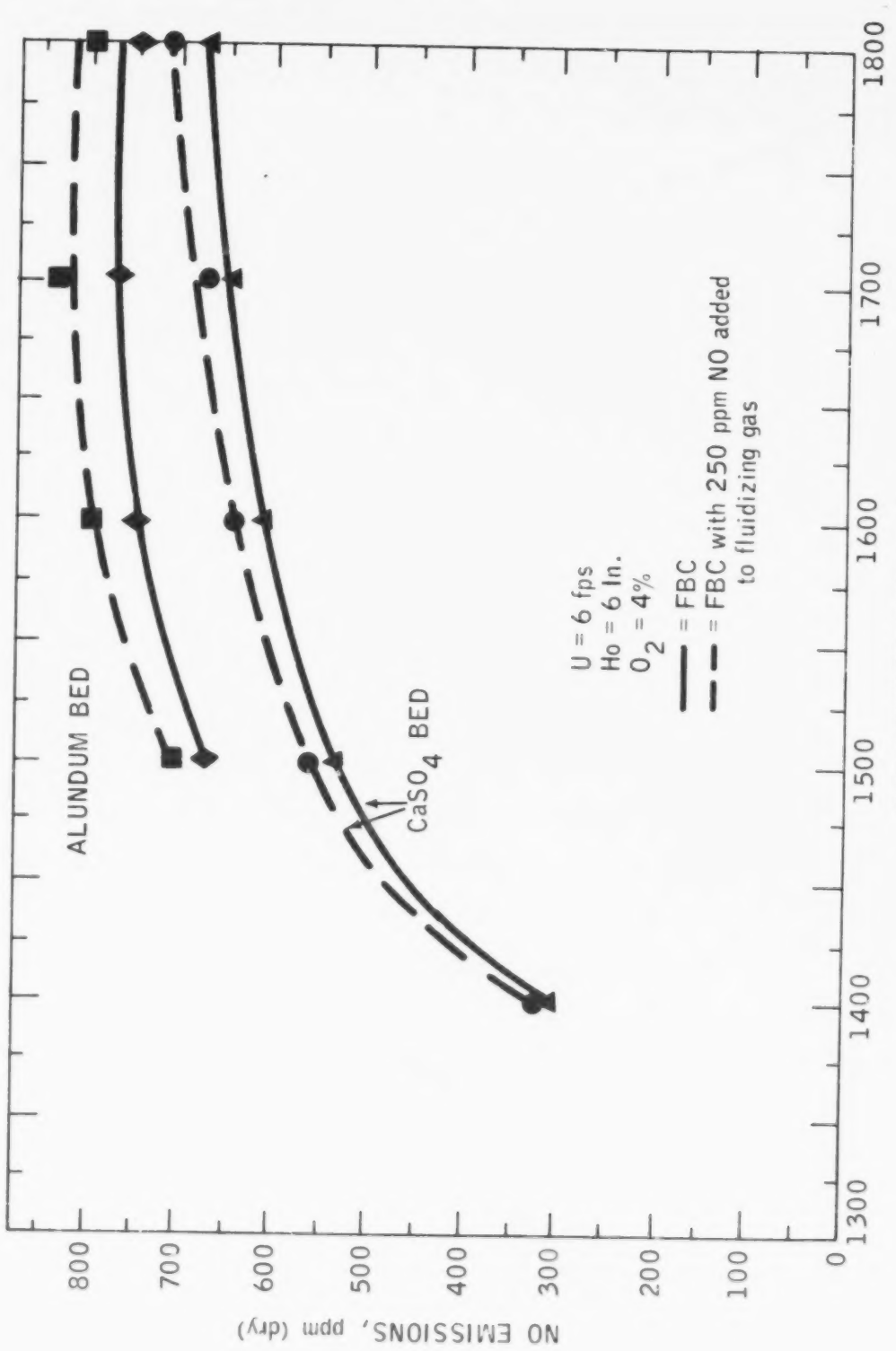


Figure 2-8

NO EMISSIONS AS A FUNCTION OF BED TEMPERATURE



One possible explanation for this apparent acceleration at low temperatures stems from the observation that the CO emissions increased in these experiments as bed temperature was decreased. The CO emissions were 250 ppm at 1800°F and 5200 ppm at 1400°F. Therefore, it is likely that the lower NO emissions obtained with $CaSO_4$ (as compared to Alundum) could have been the result of the reduction of NO by CO, with $CaSO_4$ acting as the catalyst. Although a similar surface reaction could also be occurring over the Alundum, the much lower surface area of the Alundum would not be expected to cause any significant catalytic enhancement of the reaction.

In order to obtain additional information on the effect of temperature on the formation of NO_x in the fluidized bed combustor, experiments were performed adding 250 ppm NO to the fluidizing gas of the Esso FBC for each of the bed temperatures examined. The concentrations of NO in the flue gas following this addition are shown in Figure 2-8, by the dashed lines. The increase in NO concentration in the flue gas (following NO addition to the fluidizing gas) was generally small, indicating that much of the 250 ppm NO added to the fluidizing gas had reacted as it passed through the reactor.

In order to compare the fate of the nitrogen in the fuel to the fate of the nitrogen added as NO, the following calculations were made:

1. The fractional conversion of fuel N to NO was calculated.
2. The fractional conversion (retention) of added N (as NO) to NO was calculated.

Both of these calculations are illustrated in Appendix 5.

As shown in Figures 2-9 and 2-10, the fractional conversion of fuel nitrogen to NO was consistently greater than the fractional conversion of the added nitrogen to NO (i.e. more decomposition or reduction of the added NO occurred). This result is believed to reflect the greater reduction of the NO added to the fluidizing air as it passed through the highly reducing zone that existed above the grid of the Esso FBC. This reducing zone existed because the coal was fed to the bed at single point in this unit, i.e., through the center of the grid. This implies that increasing the number or extent of localized reducing zones within the bed would cause a decrease in NO emissions.

3.1.2 Excess Air

The NO emissions from the Esso FBC were determined as a function of the excess air level used for the combustion over the range of 1 to 8 percent O_2 in the flue gas, using Alundum and $CaSO_4$ as bed materials. The complete results of this set of experiments are given in Appendix 4. The actual and normalized (3% O_2) emissions are shown as a function of percent O_2 in the flue gas in Figures 2-11 and 2-12 for Alundum and $CaSO_4$ beds, respectively.

Figure 2-9

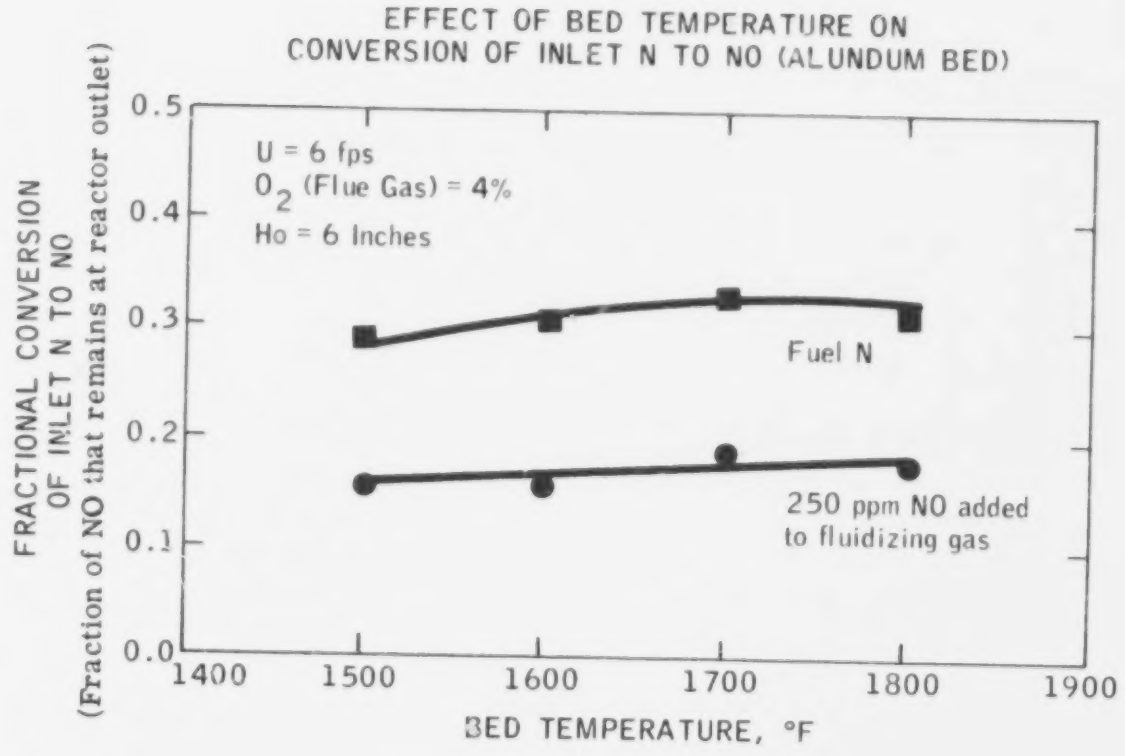


Figure 2-10

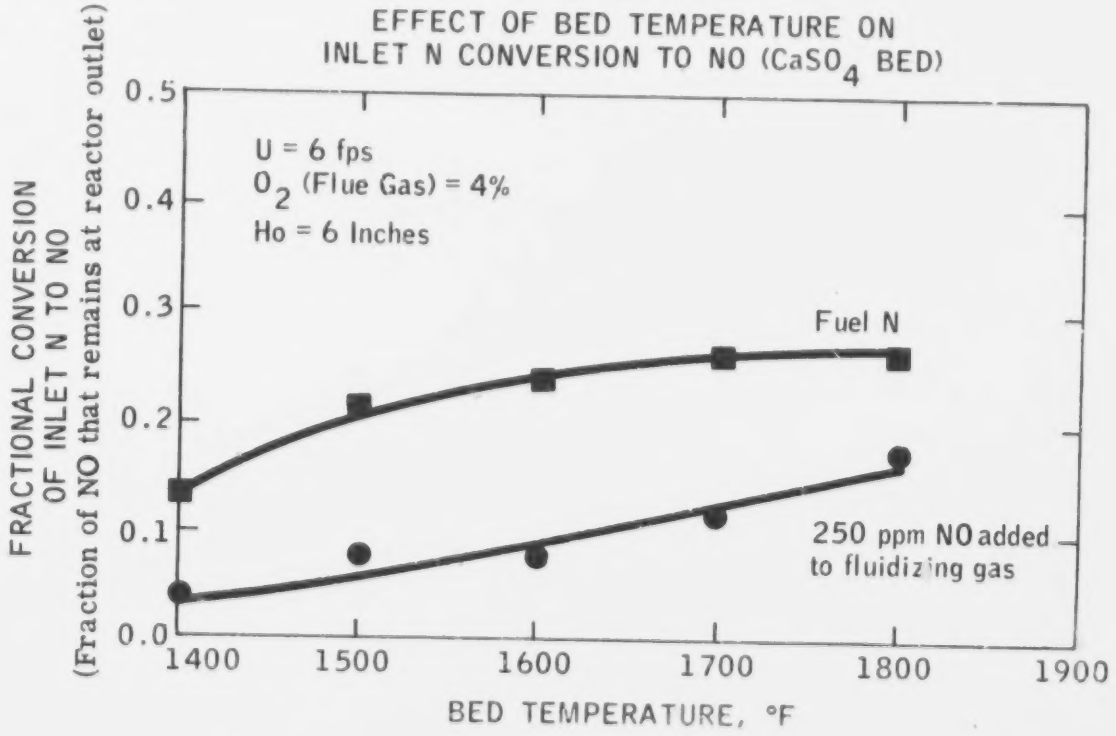


Figure 2-11

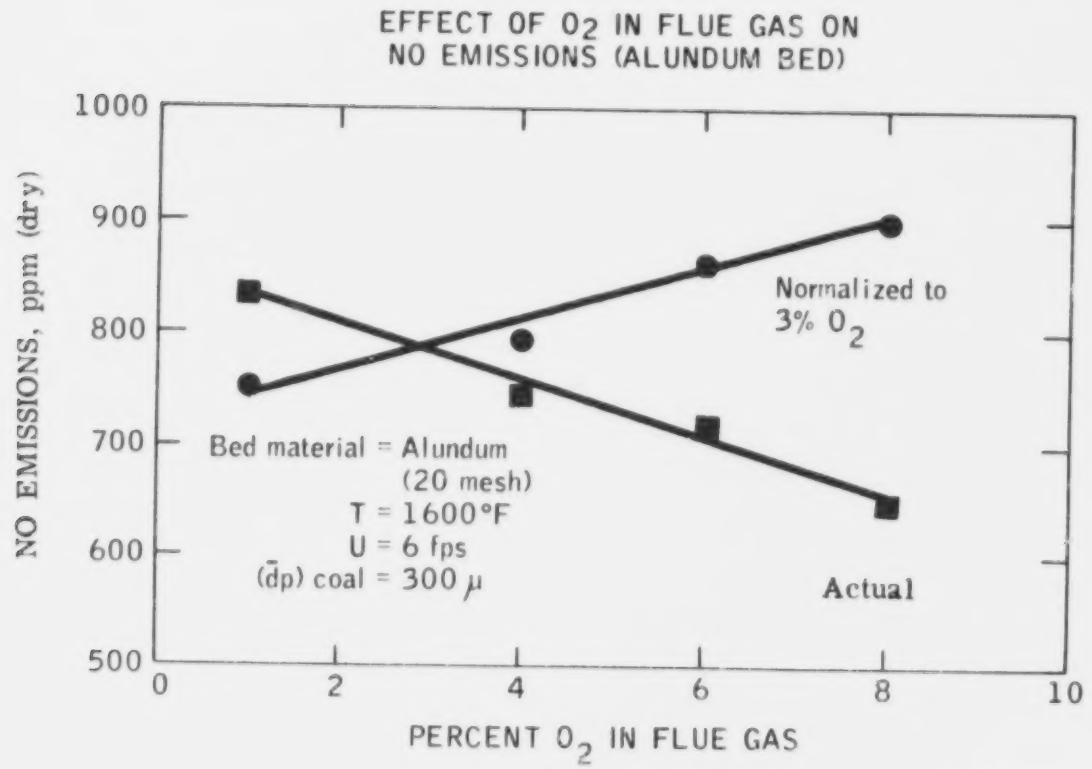
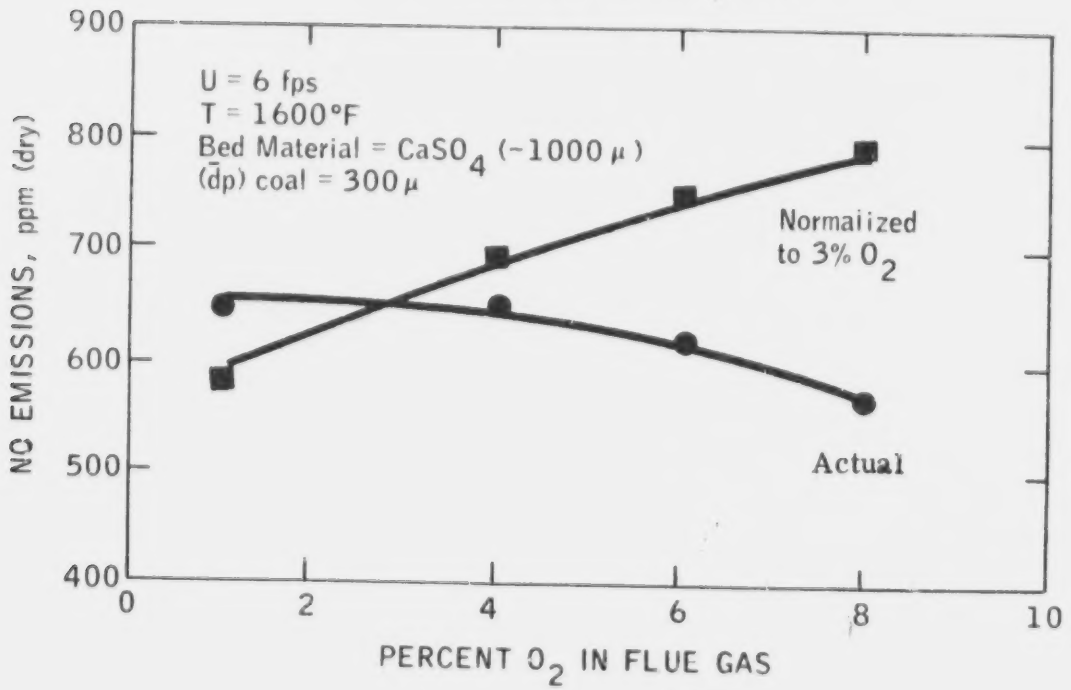


Figure 2-12

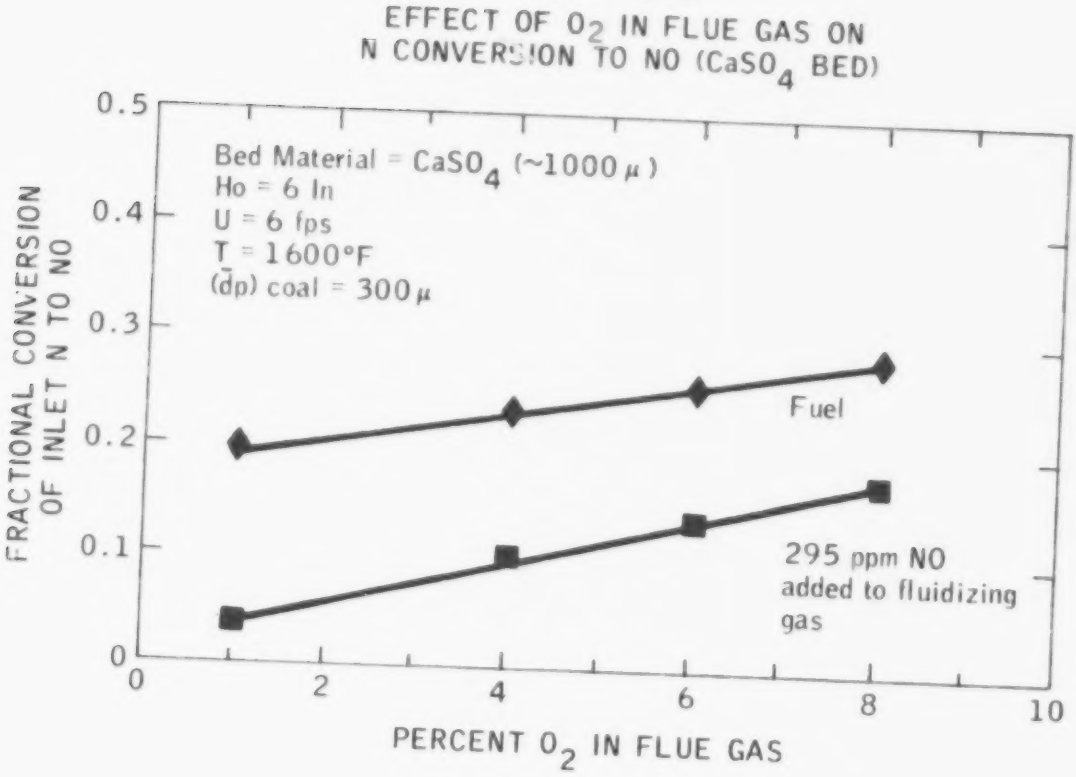


Actual NO emissions, using both Alundum and $CaSO_4$ as bed materials, decreased as excess air (percent O_2) was increased. However, when the emissions were normalized to a constant gas volume (3% O_2), the NO emissions increased as the excess air was increased. The NO formation rate was thus increased by the higher average oxygen concentration in the bed.

The NO emissions were consistently lower over the $CaSO_4$ bed, as compared to the Alundum bed, which confirmed the previous observation that greater reduction of NO was occurring over $CaSO_4$ compared to Alundum. The difference in the NO emissions from the two beds, Alundum and $CaSO_4$, increased as the excess air was decreased. Also, the CO concentration in the flue gas increased as excess air was decreased. This result lent further support to the postulate that NO and CO were reacting over $CaSO_4$ and that the rate of this reaction would be increased by high CO concentrations.

To further examine the effect of O_2 level on NO emissions, 295 ppm of NO was added to the fluidizing gas in experiments with the $CaSO_4$ bed. The flue gas NO concentrations following this addition are given in Appendix 4. The fractional conversion of fuel nitrogen to NO (before addition) and the fractional conversion of added nitrogen (as NO) to NO are shown in Figure 2-13. The high reduction of the NO added to the fluidizing gas again reflects the passage of this gas through the highly reducing zone above the grid.

Figure 2-13


EFFECT OF O_2 IN FLUE GAS ON
N CONVERSION TO NO ($CaSO_4$ BED)
Bed Material = $CaSO_4$ (~1000 μ)
Ho = 6 In
U = 6 fps
T = 1600°F
(d̄p) coal = 300 μ
Fuel
295 ppm NO
added to fluidizing
gas
FRACTIONAL CONVERSION
OF INLET N TO NO
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10
PERCENT O_2 IN FLUE GAS

3.2 NO-CO Reaction Studies

The observed effects on NO emissions produced by varying the excess air level, the combustion bed temperature, and the fluidizing bed material indicated that part of the NO formed by oxidation of the nitrogen in the coal was being reduced in the bed--most probably by the CO that was known to be present from analyses of the flue gases. To confirm this, and to investigate the characteristics of the NO-CO reaction and its catalysis by $CaSO_4$ and CaO, two series of experiments were made in the fixed bed reactor system described in Section 1.2. The first of these was made using the 2.25 inch ID ceramic reactor, with different concentration of NO and CO blended with nitrogen and passed through beds of $CaSO_4$ (Drierite). Results of this series of experiments are summarized in Table 2-3. Negligible reaction occurred when the simulated gas was passed through the reactor containing only the alumina bed support.

Table 2-3

Differential Reactor Results of
$NO-CO-CaSO_4$ Reaction System

Reactor = 2.25 inch ID ceramic tube
Bed Material = $CaSO_4$
Bed Weight = 75 grams
Gas Velocity = 2 fps

Run Number	40-A	40-B	37-A	37-B	38-A	38-B
Bed Temperature, °F	1300	1300	1500	1500	1700	1700
Gas Volume, CFM	0.99	0.99	0.90	0.90	0.81	0.81
Inlet Gas Composition						
NO, ppm	2017	2017	1990	1990	2025	2025
CO, ppm*	----	----	----	----	----	----
N_2	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Outlet Gas Composition						
NO, ppm	2000	1959	1952	1865	1980	1912
CO, ppm	1700	3425	1670	3670	1720	3180
N_2	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

* not measured

From the results summarized in Table 2-3, reaction rates were calculated and are shown in Figure 2-14 as a function of the reciprocal absolute temperature. The reaction rate is seen to exhibit an Arrhenius type dependence on temperature. The apparent activation energy derived from these experimental results is 8.5 kcal g. mole and 6.5 kcal per g. mole for outlet concentrations of 3400 ppm and 1700 ppm respectively. From these very limited data, the NO-CO reaction rate appears to depend on the square of the CO concentration (i.e., is 2nd order in CO concentration) since the rates measured at 3400 ppm outlet concentration averaged about four times those obtained at 1700 ppm.

Additional information relating to the order of the CO-NO reaction was obtained in a second series of fixed bed experiments. In this series of experiments, the reaction of NO with CO was studied over calcined limestone in the 2" reactor. Three concentration levels of NO and CO in N_2 were studied - 500, 1000 and 2000 ppm. The results obtained in this series of experiments are shown in Table 2-4.

Table 2-4

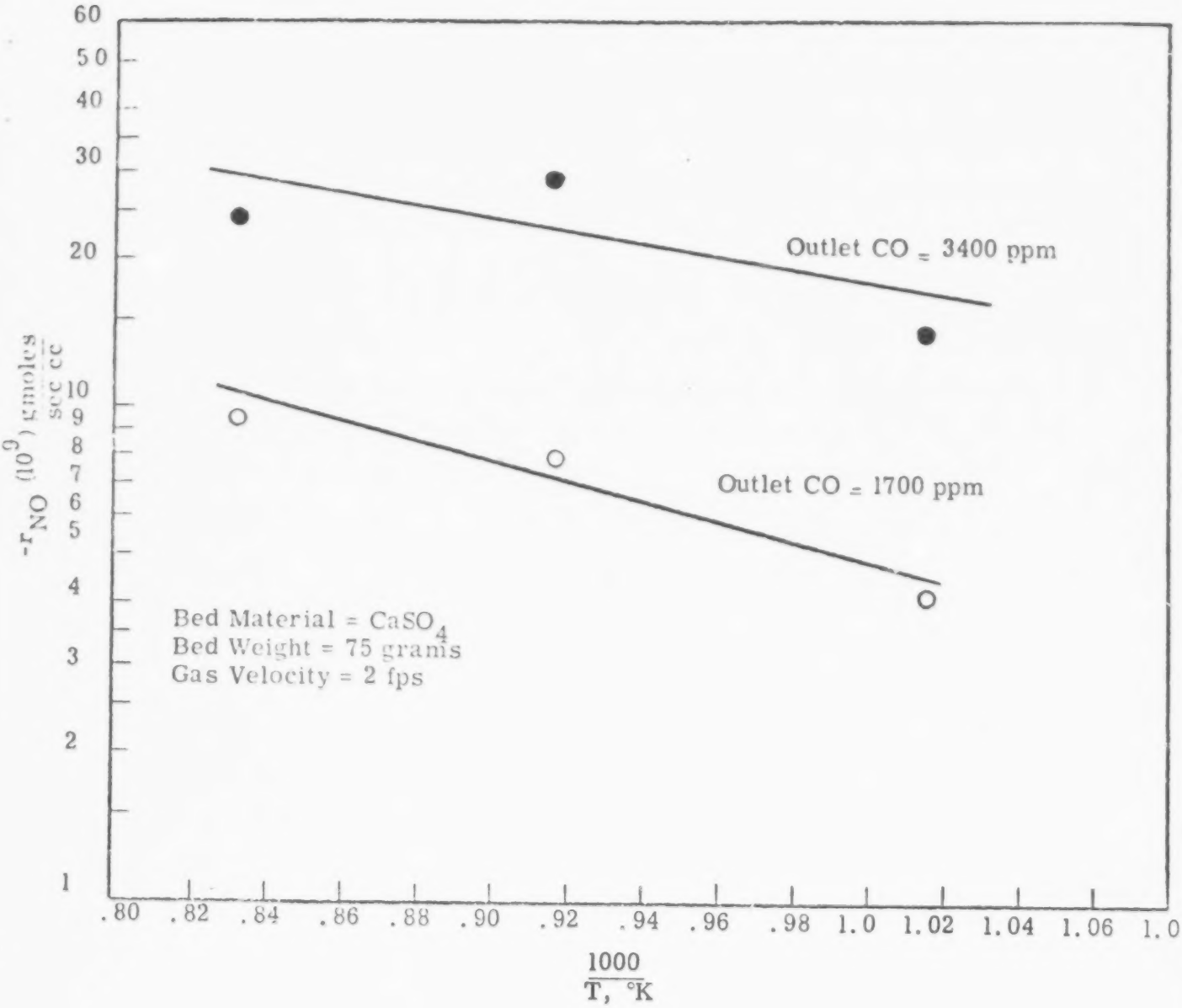
Differential Reactor Results of
NO-CO-CaO Reaction System

Reactor - 3/4 inch ID Steel Tube
Bed Material - 1359 Limestone
Bed Weight - 60 grams
Gas Velocity - 2 fps

Inlet NO Concentration, ppm	500	←	1000	→	2000
Inlet CO Concentration, ppm	1000	500	1000	2000	1000
Outlet NO Concentration, ppm	0	510	115	0	1150
Outlet CO Concentration, ppm	700	0	0	725	0

FIGURE 2-14

EFFECT OF TEMPERATURE ON THE NO-CO REACTION RATE



It can be seen that the limiting reactant was essentially completely consumed in these experiments. Also, the decreases in NO and CO concentrations were on a one for one basis. Coupled with the fact that this reaction showed a second order dependence on the CO concentration, these experiments indicated that the reaction between NO and CO proceeds by equation (2-3) rather than (2-4).

$$2\ CO + 2\ NO \longrightarrow 2\ CO_2 + N_2 \qquad (2\text{-}3)$$

$$CO + 2\ NO \longrightarrow CO_2 + N_2O \qquad (2\text{-}4)$$

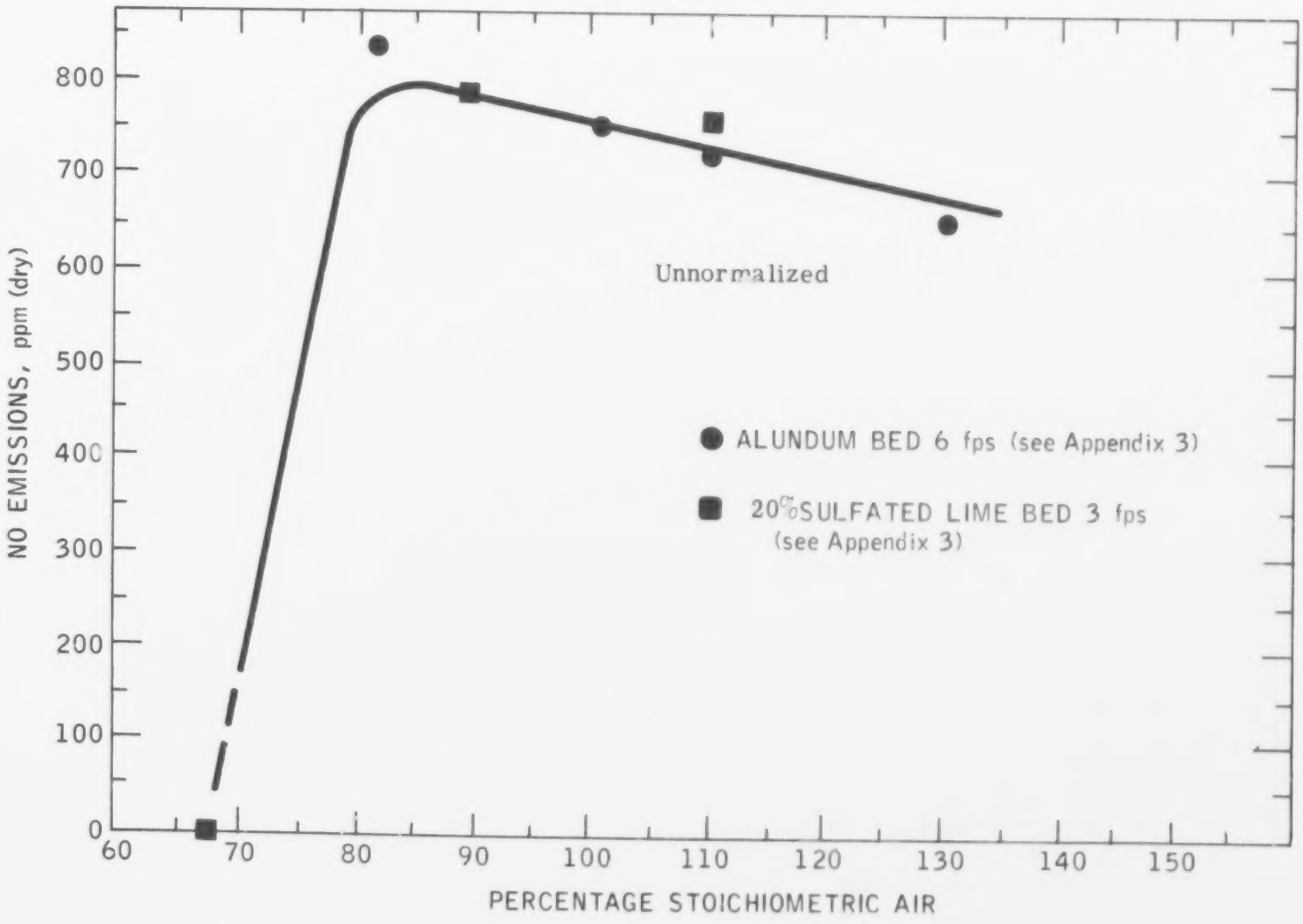
3.2.1 Effect of Sub-Stoichiometric Combustion

Having shown that the CO-NO reaction can be important in establishing the level of NO emissions obtained in the fluidized bed combustor, additional experiments were made to determine the effect of operating such a combustor with less than the stoichiometric air required for complete coal combustion. Under these conditions, NO emissions were expected to be low because of the high CO concentrations, and because oxidation of fuel nitrogen would be retarded.

The experiments that were made used a partially sulfated lime bed and stoichiometric air levels ranging from about 68% to 130%. The NO emissions obtained as a function of the stoichiometric air level are shown in Figure 2-15 and complete data for these experiments are given in Appendix 4. NO emissions are seen to fall rapidly below about the 80% stoichiometric air level and became immeasurable at the 68% level.

FIGURE 2-15

NO EMISSIONS AS A FUNCTION
OF PERCENTAGE STOICHIOMETRIC AIR



The sub-stoichiometric operations essentially simulated the first stage of a two-stage combustor. The combustible losses in these operations were high, with CO emissions being greater than 6000 ppm (range of instrument) at all conditions below 90% stoichiometric air addition. Continuous measurement with the DuPont 461 Analyzer showed negligible NO_2 emissions over the entire range of excess air levels examined.

The air level at which NO emissions were observed to decrease rapidly should depend upon the combustion efficiency attained, which, in turn, is dependent upon operating variables such as bed temperature and superficial gas velocity. The combustion efficiencies for the data shown in Figure 2-15 were generally below that possible for complete utilization of the available oxygen. Higher combustion efficiencies would probably shift the entire curve shown in this figure to the right.

3.2.2 Effect of H_2O on the NO-CO Reaction

A final series of experiments on the NO-CO reaction was made to determine the effect of water vapor on the reaction. The 2.5 inch electrically heated reactor was used for these experiments. NO, CO and N_2 cylinder gases were blended and steam was added to give the desired reactor inlet gas concentration. The results of these experimen.s are given in Table 2-5.

Table 2-5

Results of Study of NO-CO-H_2O Reaction System

Run No.	37-A	37-B	37-C	38-A	38-B	38-C	39-A	39-B	41-A	41-B
Bed Material	$CaSO_4$	$CaSO_4$	$CaSO_4$	$CaSO_4$	$CaSO_4$	$CaSO_4$	Alumina	Alumina	None	None
Bed Temp, °F	1500	1500	1500	1700	1700	1700	1500	1500	1500	1500
Inlet Gas Volume, CFM	0.90	0.935	0.97	0.81	0.84	0.87	0.90	0.97	0.90	0.97
Inlet Gas Composition										
NO, ppm (dry)	1990	1990	1990	2025	2025	2025	2010	2010	2035	2035
CO, ppm (dry)	4000	4000	4000	4000	4000	4000	4000	4000	4000	4000
H_2O, %	0	3.7	7.2	0	3.9	7.3	0	7.2	0	7.2
N_2	bal	bal	bal	bal	bal	bal	bal	bal	bal	bal
Outlet Gas Composition (dry)										
NO, ppm (dry)	1915	1730	1745	1900	1575	1575	1990	1750	2015	1725
CO, ppm (dry)*	-	-	-	-	-	-	-	-	-	-
H_2O, %**	-	-	-	-	-	-	-	-	-	-
N_2	bal	bal	bal	bal	bal	bal	bal	bal	bal	bal
Fractional Conversion of NO, %	3.8	13.0	12.3	6.2	22.2	22.2	1.0	13.0	0.5	15.2

* Not measured.

** Not measured, gas passed through 35°F refrigerator before analysis.

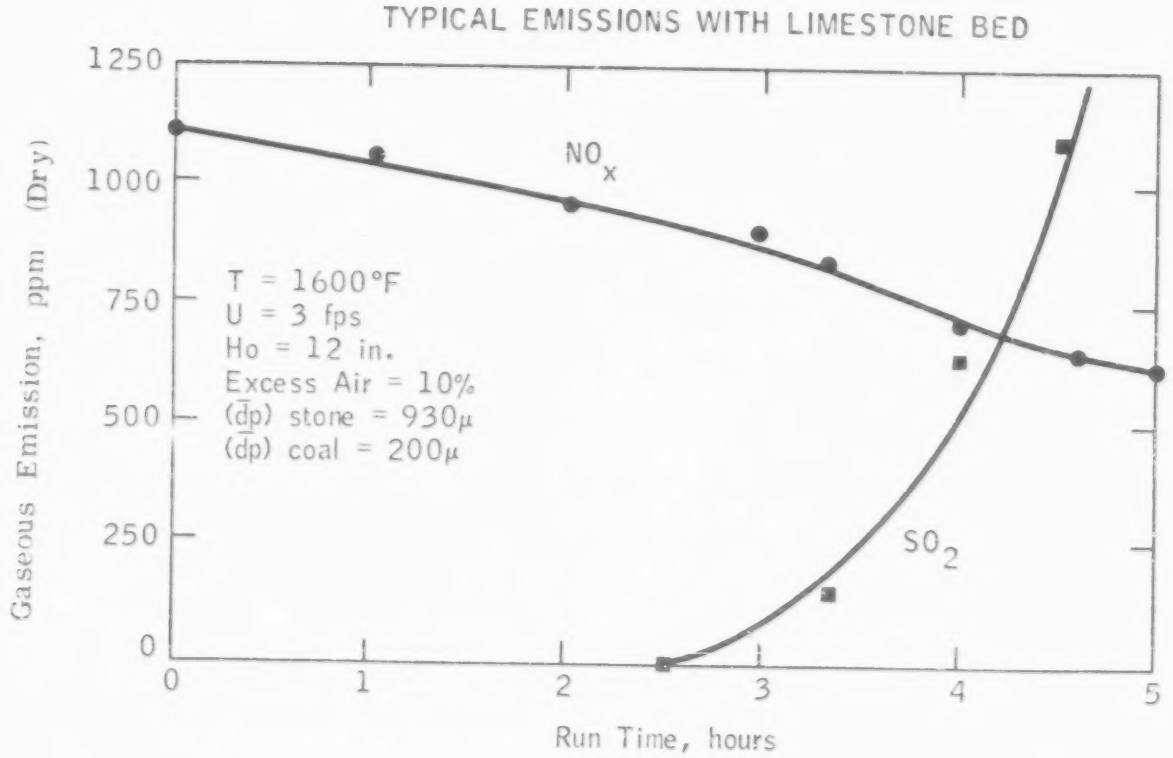
The addition of a few percent steam (3.7%) is seen to enhance the CO reduction reaction. Higher concentrations of steam (i.e., 7.2%) do not increase the NO conversion and may in fact decrease it slightly. Runs 38 A, B and C show the effect of reactor temperature on the NO conversion in the presence of the water. The increase in temperature from 1500 to 1700°F about doubled the fractional conversion of NO with the steam present but had very little effect without the steam. This confirms the low activation energy noted in Section 3.2 for the NO-CO reaction when it occurs in the absence of steam.

Runs 39 and 41 show that the addition of steam to the system minimizes the effect and the need for an active solid to promote the NO-CO reaction. Whereas in the absence of steam (Run 39A and 41A vs 37A), the alumina supports and the empty reactor gave less conversion than obtained with the $CaSO_4$, about the same NO conversion level occurred with the empty reactor and the alumina supports when steam was present. These results would indicate that the accelerating effect of steam on the rate of NO conversion is probably a gas phase reaction, or a reaction catalyzed by the wall of the ceramic reactor itself.

3.3 $NO-SO_2-CaO$ Reaction System

Typical emissions of NO and SO_2 obtained in the Esso FBC are shown in Figure 2-16. The change in SO_2 emissions reflect the batch nature of this reaction system; the bed was batch charged with lime, and coal was continuously fed. Initially, the reactivity of the lime was high enough that essentially no SO_2 appeared in the flue gas. As the run progressed, the lime reacted with SO_2 to form $CaSO_4$, and eventually the $CaSO_4$ concentration became great enough that not all of the SO_2 was captured by the lime and SO_2 appeared in the flue gas.

Figure 2-16



In order to obtain further information on this reaction system, a differential reactor study was made. The fixed bed reactor system shown in Figure 2-4 was used in this study. Premixed cylinders of NO in N_2 (at different concentrations) were used to assure uniformity of inlet concentration. Pure SO_2 was added to the inlet gas as desired. The dilution effect of the added SO_2 was negligible. Complete results of These experiments are given in Appendix 6. These experiments again showed that no reaction occurred between NO and SO_2 over $CaSO_4$ or Alundum. A reaction did occur over partially-sulfated lime. The apparent order and the temperature dependence for this reaction are given in Sections 3.3.2 and 3.3.3. The characteristics of the partially-sulfated lime used are given in Appendix 7.

3.3.1 Examination of Rate Controlling Mechanism in the $NO-SO_2-CaO$ Reaction System

Fixed bed reaction studies were made in the 2-1/2 inch externally heated unit to determine if gas film diffusion was the controlling factor in the $NO-SO_2-CaO$ reaction system. In these experiments, the (weight of bed material)/(inlet gas volume) ratio was maintained constant at different bed weights. In the region in which gas film diffusion is <u>not</u> controlling, the fractional conversion of the reactants should be constant in such a series of experiments (5). As shown in Table 2-6, the fractional conversion of inlet NO was essentially constant in the experiments conducted, indicating that gas film diffusion was not controlling. The higher conversion obtained with the smaller bed probably reflects the fact that the upper surface of this bed was not restrained, allowing for some expansion. The temperature within the deeper fixed bed, measured at two axial positions and two radial positions, was 1475 $\pm$ 50°F.

Table 2-6

Conversion of NO at Constant W/F
Indicates Film Diffusion Not Controlling

Bed Temperature = 1500°F
Inlet NO = 580 ppm
Inlet = 1900 ppm
Bed Material = 16.6% Sulfated Lime

Run Number	W, Grams	F, cfm	W/F, grams/CFM	X
10	150	0.90	167	0.43
13	300	1.80	167	0.37

As shown in Figure 2-16, NO emissions from the Esso FBC were typically above 1000 ppm at the start of the run, but decreased as the run progressed. Since the only two factors that changed with time were the increase in SO_2 concentration and the sulfation level of the lime, it appeared that one or both of these changes were causing the downward trend observed in NO emissions.

With the objective of pinpointing the cause for the downward trend in NO emissions, a number of experiments were made with different bed materials in the 2.5" fixed bed reactor shown in Figure 2.4. Gases containing NO and SO_2 diluted with nitrogen were used for these experiments. To determine the extent of reaction, if any, occurring in the gas phase, one experiment was carried out without any bed material present in the reactor. A summary of the results of these experiments is given in Table 2-7.

Table 2-7

Effect of Bed Material
on the $NO-SO_2$ Reaction

Reactor Temperature - 1600°F; Superficial Gas Velocity - 2 fps;
Settled Bed Height - Approximately 6 In.

Bed Material	NO_x Conc., ppm Before SO_2 Intro.	NO_x Conc., ppm After SO_2 Intro.	SO_2 Conc., ppm Inlet	SO_2 Conc., ppm Outlet
	Transport Gas - N_2			
1. Gas Phase	900	900	1290	1290
2a) Partially-Sulfated Lime*	840	440	785	300
b) Partially-Sulfated Lime*	830	180	1510	480
3. Alundum	820	820	1000	1000
4. $CaSO_4$ (Anhydride)	860	860	670	670

* From the Esso FBC.

These results showed that NO and SO_2 did not react in the gas phase, over Alundum or over $CaSO_4$ at the conditions examined. However, a reaction did occur with partially-sulfated lime. The rate of this reaction increased with increasing SO_2 concentration. Therefore, it appeared that the $NO-SO_2$ reaction system involved CaO.

3.3.2 Apparent Reaction Order with Respect to NO

In order to determine the apparent order of the $NO-SO_2$ reaction, additional fixed bed reaction studies were carried out with the 2-1/2 inch reactor. Premixed cylinders of NO in N_2 at concentrations of 2110 ppm, 1035 ppm and 485 ppm were used for these studies. The concentration of the cylinder gas was analyzed, and then flow to the hot reactor initiated. The reactor outlet NO concentration was measured. On attaining a steady state condition, SO_2 was blended to the inlet gas at the desired concentration and the outlet NO and SO_2 concentrations were monitored.

The apparent order of the reaction with respect to NO was determined by assuming the rate equation to be of the form given in equation (2-5).

$$- r_{NO} = - \frac{1}{W} \frac{d(NO)}{dt} = k(NO)^n \ (SO_2)^m \qquad (2\text{-}5)$$

If the SO_2 concentration is assumed to be greatly in excess of the NO concentration and therefore to be constant, the apparent order of the reaction system with respect to NO can be determined by plotting ln $(-\frac{1}{W}\frac{d(NO)}{dt})$ versus ln (NO). The experimental results plotted this way are shown in Figure 2-17. The SO_2 concentrations shown are the arithmetic averages of the inlet and outlet SO_2 concentrations. The apparent order of the reaction (i.e., the slopes of the curves) was 0.53 at an average SO_2 concentration of about 550 ppm and 0.67 at an average SO_2 concentration of about 1650 ppm.

An order of approximately 0.5 is consistent with a Langmuir-Hischelwood mechanism (6) for a single reactant absorbing on an active site. The rate equation for this mechanism is given by:

$$-r_{NO} = \frac{kKNO}{1 + KNO} \qquad (2\text{-}6)$$

This equation can be approximated by:

$$-r_{NO} + k(NO)^n \quad \text{where } 0<n<1 \qquad (2\text{-}7)$$

At high NO concentration where $KNO \gg 1$, equation (2-6) becomes zero order while at low concentration where $KNO \ll 1$, it approaches a first order reaction. A 0.5 order reaction is also consistent with a system in which two adjacently absorbed NO molecules react, with the following rate equation being applicable (6):

$$-r_{NO} = \frac{kK(NO)^2}{(1 + KNO)^2} \qquad (2\text{-}8)$$

or first approximation

$$-r_{NO} = k(NO)^n \qquad \text{where } 0<n<2 \qquad (2\text{-}9)$$

A 0.5 order is not consistent with a Langmuir-Rideal mechanism, in which one NO molecule is physically absorbed on the surface, and the absorbed molecule then reacts with a gas phase molecule. The rate equation for this mechanism is as follows (6):

$$-r_{NO} = \frac{kK(NO)^2}{1 + K(NO)} \qquad (2\text{-}10)$$

or first approximation

$$-r_{NO} = k(NO)^n \qquad \text{where } 1<n<2$$

The rate data obtained are thus consistent with an overall reaction scheme involving NO, SO_2 and CaO as represented by equations (2-11) and (2-12).

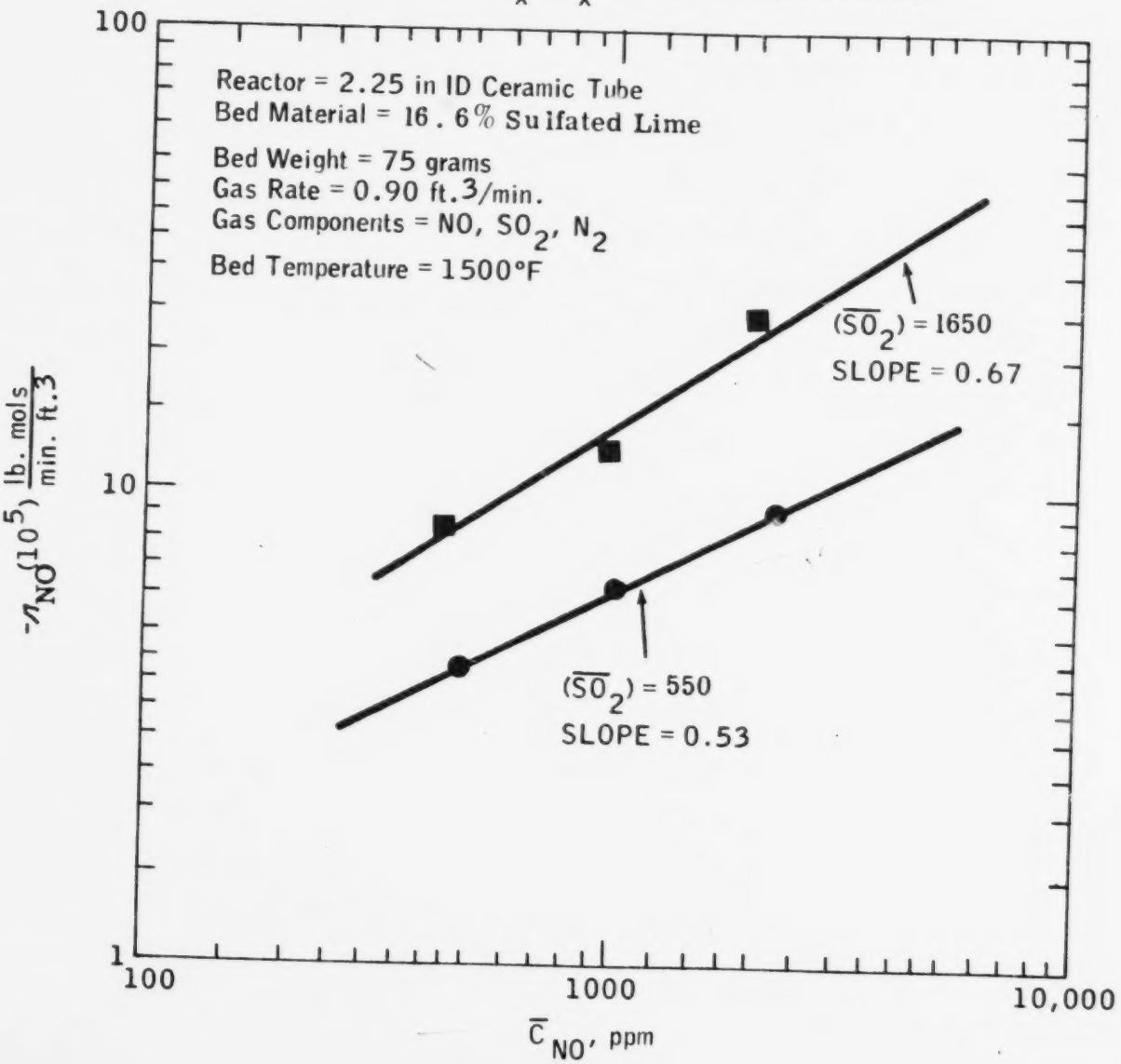
$$CaO + SO_2 \longrightarrow CaSO_3 \qquad (2\text{-}11)$$

$$2CaSO_3 + 2NO \longrightarrow 2CaSO_4 + N_2 \qquad (2\text{-}12)$$

where it is assumed that CaO and SO_2 react to form $CaSO_3$, which then acts as an active site for converting the NO to N_2.

Figure 2-17

APPARENT REACTION ORDER WITH RESPECT TO NO OF NO_x-SO_x-CaO REACTION SYSTEM



3.3.3 Temperature Dependence of $NO-SO_2-CaO$ System

The temperature dependence of the $NO-SO_2-CaO$ reaction system was next examined in the 2-1/2 inch fixed bed unit over the temperature range from 1400°F to 1600°F. The results of these experiments are given in Appendix 6. As shown in Figure 2-18, this reaction system demonstrated a negative temperature dependence in the range of 1400°F to 1600°F.

This negative temperature dependence is also consistent with the reaction mechanism represented by equations (4-10) and (4-11). Since $CaSO_3$ is probably the reactive intermediate in this reaction sequence, higher $CaSO_3$ concentrations should lead to a greater rate of NO disappearance. The SO_2 concentration in equilibrium with $CaSO_3$ and CaO is given in Figure 2-19 as a function of temperature.

$$CaO + SO_2 \rightleftharpoons CaSO_3 \qquad (2\text{-}13)$$

For the inlet SO_2 concentration of 700 ppm used in this study, the equilibrium temperature from Figure 2-19 is 1430°F. This means that the $CaSO_3$ is thermodynamically stable at all temperatures below 1430°F and unstable above 1430°F. Therefore, a rapidly accelerating rate with decreasing temperature for the $CaO-SO_2-NO$ reaction system beginning at about 1400°F, would be expected.

Figure 2-18

TEMPERATURE DEPENDENCE
OF NO-SO_2-CaO REACTION SYSTEM

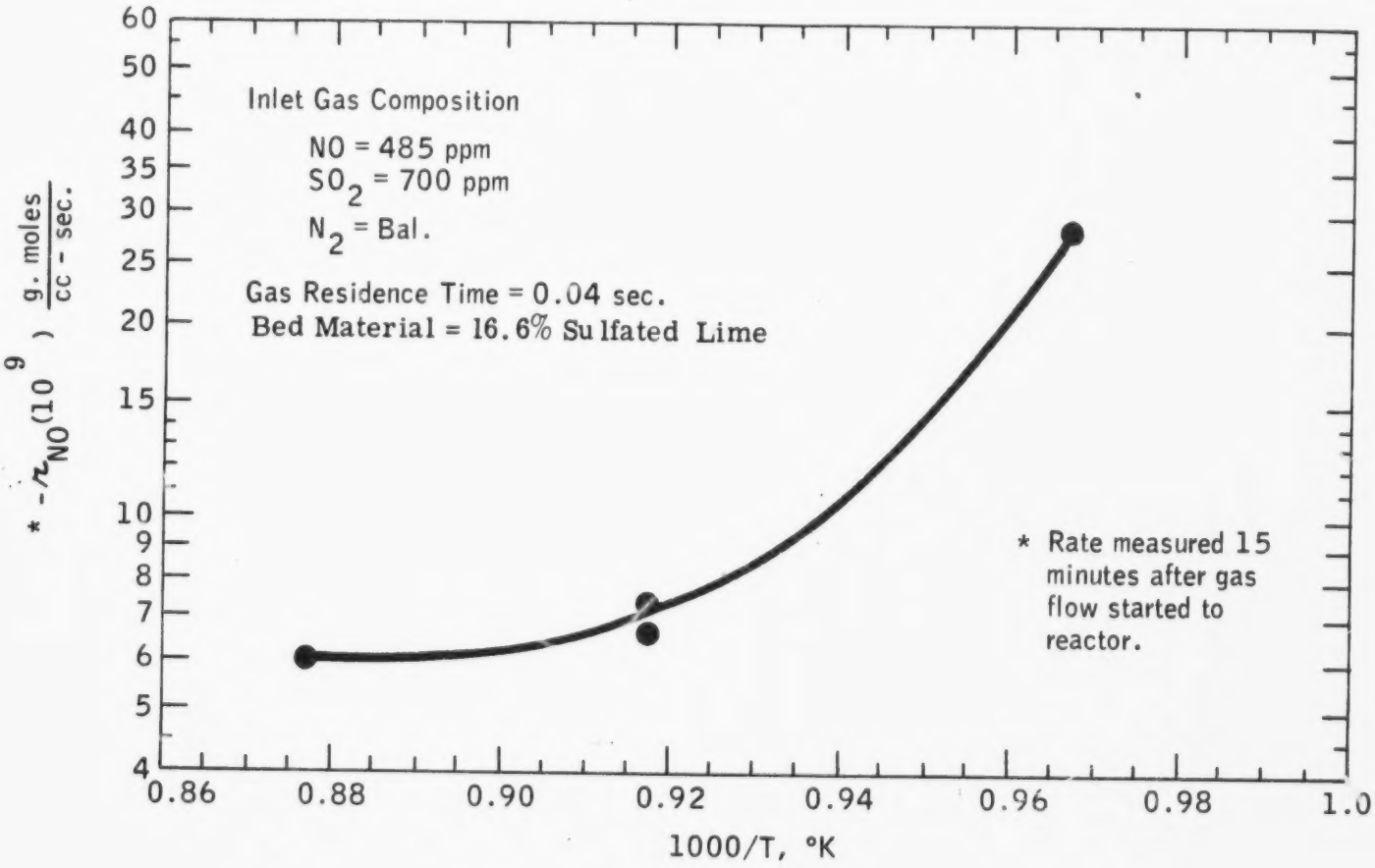
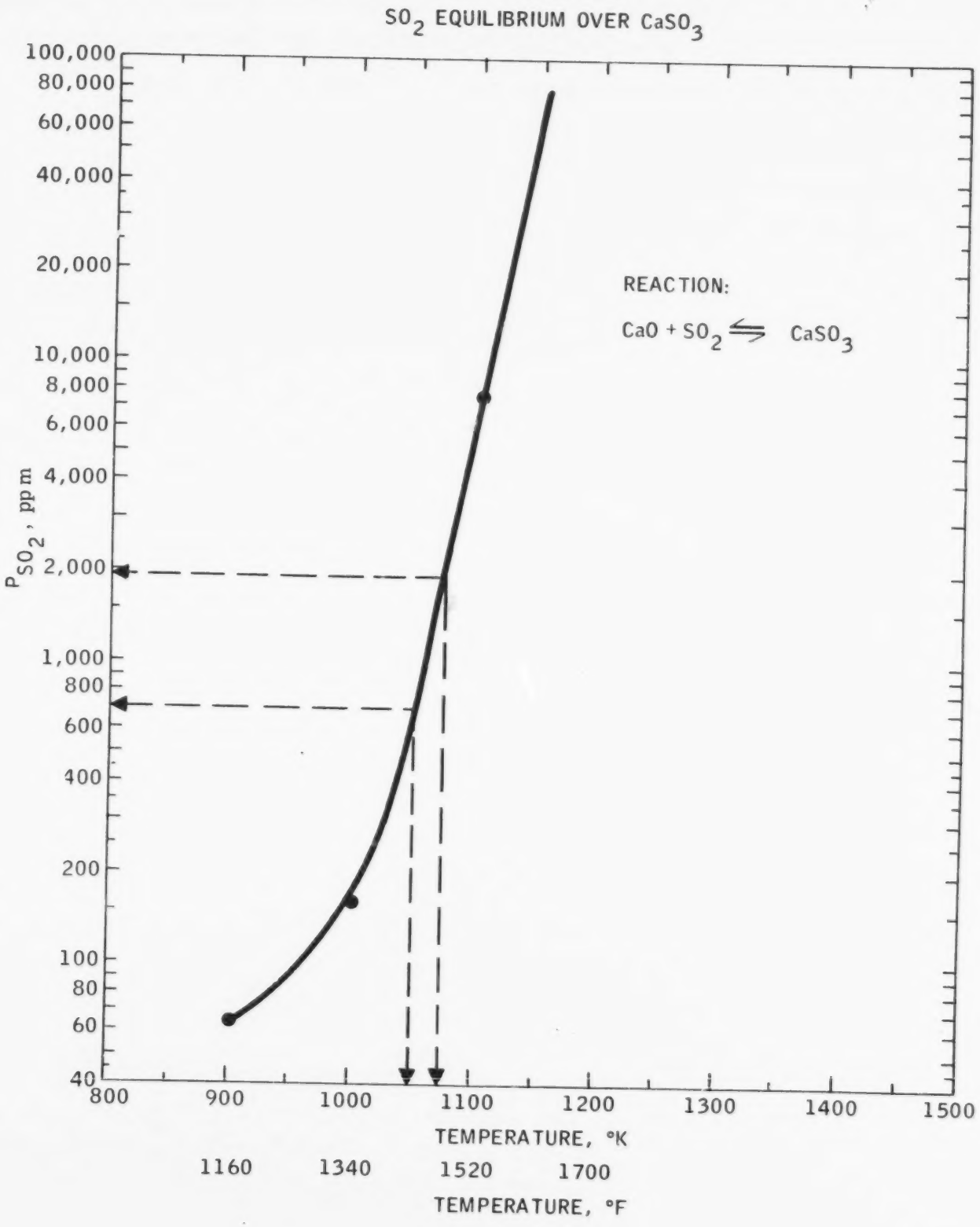


Figure 2-19


SO_2 EQUILIBRIUM OVER $CaSO_3$
100,000
80,000
60,000
40,000
20,000
10,000
8,000
6,000
4,000
2,000
1,000
800
600
400
200
100
80
60
40
P_{SO_2}, ppm
REACTION:
$CaO + SO_2 \rightleftharpoons CaSO_3$
800
900
1000
1100
1200
1300
1400
1500
TEMPERATURE, °K
1160
1340
1520
1700
TEMPERATURE, °F

3.3.4 Miscellaneous $NO-SO_2-CO-CaO$ Reaction Studies

Additional $NO-SO_2-CaO$ reaction experiments were made using the 1 inch fixed bed reactor system described in Section 1.2.2. Gases containing 1000 ppm NO, and 500, 1000 and 2000 ppm SO_2 in N_2 were used in these experiments carried out at 1600°F. Results are summarized in Table 2-8.

Table 2-8

Additional Fixed Bed
$NO-SO_2-CaO$ Reaction Studies

Reactor	= 3/4 inch ID
Bed Material	= -16 to +18 mesh CaO
Bed Weight	= 60 grams
Gas Velocity	= 2 fps
Reaction Temperature	= 1600°F

Reactor Inlet Concentration, ppm			
NO	←	1000	→
SO_2	500	1000	2000
Reactor Outlet Concentration, ppm			
NO	650	550	380
SO_2	10-25	15-70	40-210

A comparison of these results with those obtained for the CO-NO reaction carried out in the same unit and under the same conditions (see Table 2-8 in this section) shows that the reaction of NO with CO is faster than is its reaction with SO_2, at least in the absence of moisture. This can be seen by comparing corresponding outlet NO levels at the 1000 ppm inlet NO concentration for the tests made with the 500 and 2000 ppm concentrations of CO and SO_2.

In the final studies made with the 1 inch fixed bed reactor system, evidence that CaS may play a role in the reduction of NO was obtained by reacting CaO sequentially with SO_2, then CO, and then NO. The results from this experiment are shown in Table 2-9. The NO emissions observed after subjecting the CaO to 2000 ppm of SO_2 followed by 2000 ppm of CO remained below the inlet NO concentration of 1000 ppm for over two hours after the flow of CO had been discontinued. This may reflect a reduction of NO by the CaS formed from the reaction of $CaSO_3$ with CO as shown below:

$$CaO + SO_2 \longrightarrow CaSO_3 \qquad (2\text{-}14)$$

$$CaSO_3 + 3\ CO \longrightarrow CaS + 3\ CO_2 \qquad (2\text{-}15)$$

$$CaS + 3\ NO \longrightarrow CaSO_3 + \frac{3}{2} N_2 \qquad (2\text{-}16)$$

Table 2-9

NO-CO-SO_2-CaO Reaction Studies.
Operating Conditions - Same as Table 2-8

Step #	Time Period, Min.	Inlet Gas, ppm.		Outlet Gas, ppm.		Remarks
1	0-60.	2000.	SO_2	0-225.	SO_2	Gradual increase over period.
2	60-75.	2000.	CO	0.	CO	Rapid increase from 0.-1150 ppm CO
	75-120	2000.	CO	1150.-1500.	CO	During this period SO_2-0.
3	120-160.	1000.	NO	0.	NO	Rapid increase from 0.-470. ppm NO
	160-240.	1000.	NO	470.-800.	NO	During this period SO_2- 0. for 25 min. 0.-250. For 25 min. 250.-100. For 15 min. 100.-0. For 55 min. CO - 0.

3.4 Examination of Two Stage Combustor Operation for NO_x Emissions Control

The experimental data obtained in this program indicate that at least two reactions systems are important in determining the NO_x emissions from a fluidized bed combustor. One involves the reaction of NO, SO_2 and CaO. The experimental data indicate that this reaction proceeds through a $CaSO_3$ intermediate. In the presence of oxygen, a competing reaction, given by equation (2-17), can occur which limits the extent of NO reduction.

$$2\ CaSO_3 + O_2 \longrightarrow 2\ CaSO_4 \qquad (2\text{-}17)$$

Therefore, to maximize NO reduction by reaction with SO_2 and CaO, it would be desirable to minimize the oxygen concentration in the FBC. The second reaction which can occur in fluidized bed combustors involves the CaO catalyzed reduction of NO by CO. Thus, it would be highly desirable to have reducing zones in the fluidized bed combustor to maximize NO_x reduction.

Both of these NO reactions would be accelerated by operating the fluidized bed combustor with staged addition of air. In this mode of operation, part of the combustion air would be supplied through the grid of the combustor and the remainder of the combustion air would be supplied at some level higher-up but still in the bed. By supplying substoichiometric air (based on the coal rate) through the grid, the lower part of the bed would necessarily be deficient in oxygen; high CO concentrations would be present. The second stage air would serve to burn out the CO and generate SO_2. Consequently, both the NO-SO_2-CaO and the NO-CO-CaO reduction systems would be operative in a two stage system.

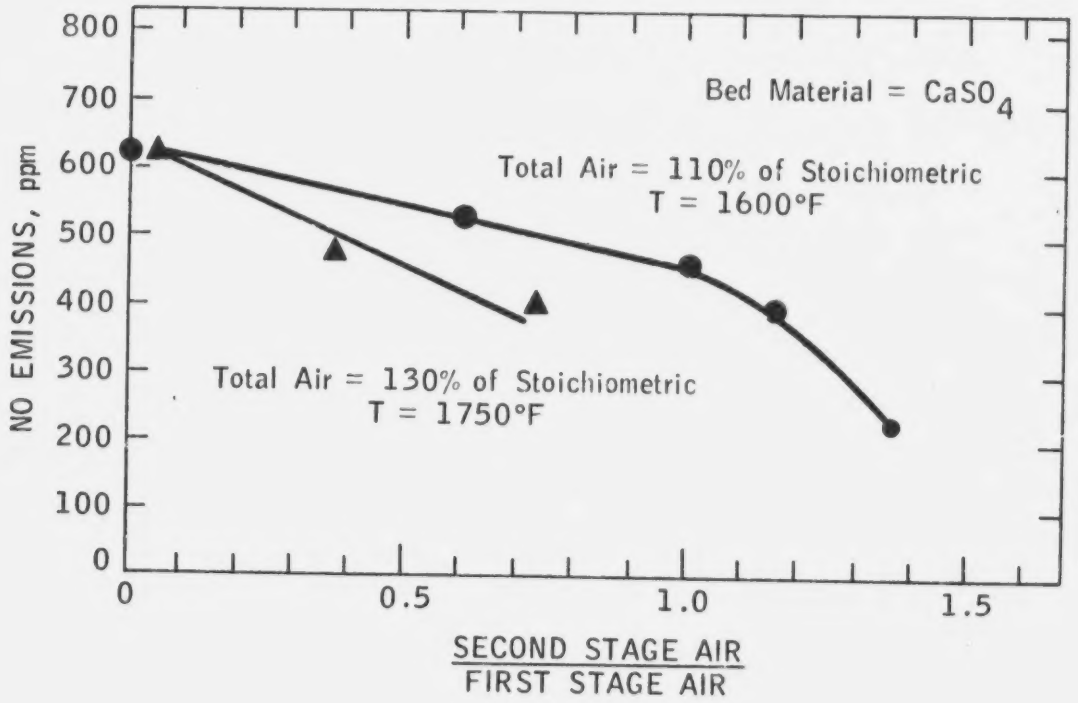
In order to verify the effectiveness of two stage combustion as a NO_x control technique, the Esso FBC was modified to allow its operation as a two stage combustor. This modification, shown in Figure 2-3, consisted of placing a 1/4 inch stainless steel tube horizontally through the bed, six inches above the grid. Holes were drilled around the upper circumference of this tube so that it acted essentially as a second air distributor.

The results of operating the Esso FBC as a two stage combustor are shown in Figure 2-20. As the ratio of the second stage air to the first stage percentage air was increased (i.e., as the first stage became more reducing), NO emissions decreased. Only two bed temperatures were examined, 1600°F and 1750°F, with the effect of staging being more pronounced at the higher temperature.

The lowest NO emissions observed in these staging runs was 200 ppm, which was achieved at 1600°F and 43 percent stoichiometric air to the first stage. Although these highly reducing first stage conditions may not be feasible for commercial operation, the potential for NO_x reduction by two stage combustion is clearly apparent. It is significant that CO emissions in all staging operations remained relatively low, at about 400 to 600 ppm.

FIGURE 2-20

STAGED FBC RESULTS



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NOMENCLATURE

atm.	Pressure in atmospheres
CMTU	Esso's Cold Model Test Unit
$\overline{dp}$	Weight Median Particle Diameter, microns
F	Inlet Gas Rate, cubic feet per minute
FBB	Fluidized Bed Boiler
FBC	Fluidized Bed Combustor
FBCR	Fluidized Bed Combustor-Regenerator (Miniplant)
fps	Feet Per Second
h	Settled Bed Height, feet
Ho	Settled Bed Height, inches
$H_{\overline{S}}$	Average Bed Slug Height, feet
k	Rate Constant
K	Absorption Equilibrium Constant
Kp	Equilibrium Constant
n, m	Reaction Orders
P	Fluidized Bed Pressure in psia
ppm	Parts Per Million
$-r_{NO}$	Rate of Disappearance of NO
$(\overline{SO_2})$	Arithmetic Average SO_2 Concentration
SCFH	Standard Cubic Feet Per Hour
SCFM	Standard Cubic Feet Per Minute
T	Bed Temperature, °F
U	Superficial Gas Velocity, feet per second
μ	Microns
v	Incipient Fluidization Velocity, feet per second
W	Bed Weight, grams
WTM	Wet Test Meter

APPENDIX 1

PREDICTED SO_2 CONCENTRATION FOR PRESSURIZED REGENERATION

The regenerator internal diameter depends on the SO_2 concentration achieved in the regenerator off-gas. Although pressurized regeneration experiments have not yet been performed, the theoretical SO_2 concentration that would be attained in the regenerator off-gas at thermodynamic equilibrium has been calculated for a number of different reducing gas compositions at 1 and 10 atmospheres. A computer program developed by the Rand Corporation (7), in which the total free energy of the reacting system is minimized, was used for these calculations. The predicted equilibrium regenerator off-gas concentrations are given in the table below for two different assumptions regarding the thermodynamic state of the solid phase. The first set of predictions assumes unit activity for each of the solid chemical species, while the second set assumes the activity of each of the solid components is proportial to its molar concentration in the total solid phase. The actual activities of the solids probably fall somewhere between these extremes.

PREDICTED EQUILIBRIUM RESULTS FOR SULFATED LIME REGENERATION AT 1 AND 10 ATMS.

Reducing Gas		1 Atmosphere			10 Atmosphere		
% CO in N_2	% CO_2 in N_2	M % SO_2 In Regen. Off-Gas	Moles $CaSO_4$/100 Moles CO converted to: CaO	CaS	M % SO_2 In Regen. Off-Gas	Moles $CaSO_4$/100 Moles CO converted to: CaO	CaS
10	10	9.1	99.6	--	8.5	94.2	--
10	20	9.0	99.4	--	8.4	92.6	--
20	20	16.6	99.3	--	9.5	53.7	10.0
		Activity of Solids $\propto$ to Concentration					
10	10	7.9	84.9	2.4	4.9	46.8	9.8
10	20	7.9	84.4	2.1	5.0	45.4	9.3
20	20	13.5	76.7	4.1	7.8	35.2	11.9

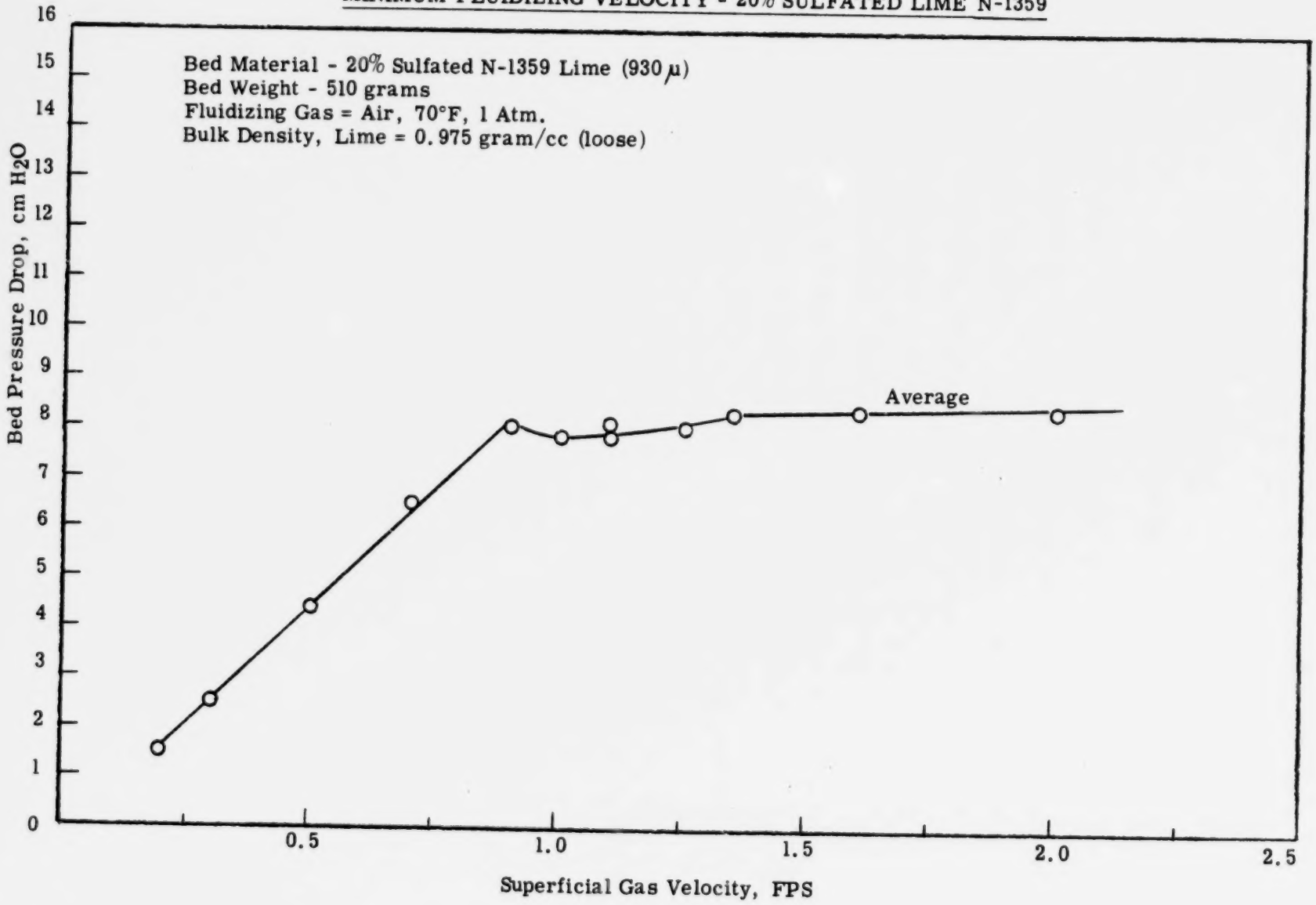
APPENDIX 2

CALCINING PROCEDURE

An electrical oven is used to calcine the limestone in this study. The oven is initially brought to 1700°F. Two thousand grams of the limestone are then charged to the oven, resulting in a settled bed of limestone approximately 1-1/2 inches in depth. A constant nitrogen bleed of four liters/minute is maintained above the bed. The system is maintained at 1700°F for seven hours, at which time the electrical heat is shut off. The oven is allowed to cool for nine hours before removing the calcined stone at 500°F. The nitrogen sweep gas is maintained during the cooling-down period.

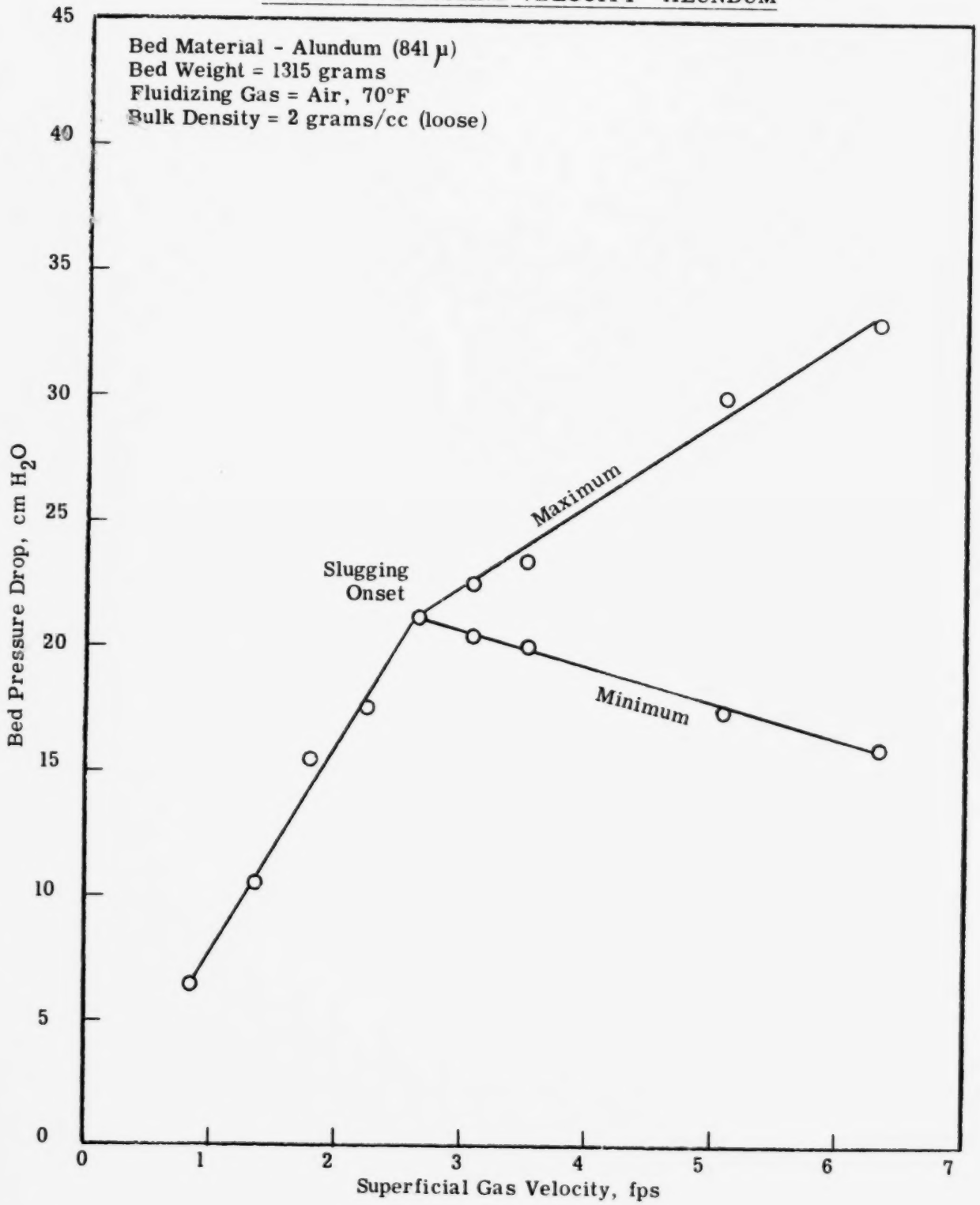
APPENDIX 3A

MINIMUM FLUIDIZING VELOCITY - 20% SULFATED LIME N-1359



APPENDIX 3B

MINIMUM FLUIDIZING VELOCITY - ALUNDUM



APPENDIX 4

Summary of Operations - Alundum and $CaSO_4$ Beds

Coal = Bit. A
Coal $\bar{d}p$ = 350 μ
Superficial Gas Velocity = 6 fps
Settled Bed height = 6 In.

Run Number	32A	32B	32C	32D
Run Length, Hrs.	1.1	1.3	1.3	1.3
Bed Material	← Alundum →			
Bed Material, $\bar{d}p$	← 840 μ →			
Bed Temperature, °F	← 1600 →			
Coal Feed Rate, lbs/hr	1.56	1.85	2.03	2.50
Air Rate, CFM	4.55	4.55	4.55	4.55
Percentage Stoich. Air	130.5	110.0	101.0	81.6
Carbon Loss in Fly Ash, %	12.6	13.4	13.1	14.3
Flue Gas Analysis (dry)				
CO_2, %	10.8	11.8	14.3	16.0
O_2, %	8.0	6.0	4.0	1.0
N_2, %	--	--	--	--
CO, ppm	450	550	1200	6000+
SO_2, ppm	2050	2325	2625	3000+
NO, ppm	650	720	750	830
NO Added to Fluidizing Gas, ppm	--	--	--	--
Flue NO After Addition, ppm	--	--	--	--
Material Balance, (Out/In) X100				
Carbon	93.6	91.5	95.6	93.8
Oxygen	102.0	97.2	103.0	100.0
Sulfur	114.0	111.0	113.0	108.0

APPENDIX 4

Summary of Operations - Alundum and $CaSO_4$ Beds (Con't)

Run Number	33A	33B	33C	33D	34A	34B	34C	34D
Run Length	1	1	1	1	1	1	1	1
Bed Material	← Alundum →				← $CaSO_4$ →			
Bed Material, $\bar{d}p$	← 840 μ →				← 1000 →			
Bed Temperature, °F	1500	1600	1700	1800	← 1600 →			
Coal Feed Rate, lbs/hr	2.20	2.02	1.75	1.63	1.57	1.83	2.07	--
Air Rate, CFM	4.78	4.55	4.33	4.14	← 4.55 →			
Percentage Stoich. Air	97.3	101	111	98.5	130.5	111.8	98.3	81.3
Carbon Loss in Fly Ash, %	17.6	14.9	13.4	10.8	12.3	12.1	11.3	13.2
Flue Gas Analysis, (dry)								
CO_2	13.6	14.4	13.7	14.0	10.5	12.0	14.1	16.2
O_2	4.0	4.0	4.0	4.0	8.0	6.0	4.0	1.0
N_2	--	--	--	--	--	--	--	--
CO	5200	1800	570	250	350	570	820	6000+
SO_2	2625	2525	2325	2250	2100	2500	2800	3000+
NO	665	750	770	745	565	620	650	650
NO Added to Fluidizing Gas, ppm	254	253	252	253	295	293	295	295
Flue NO After Addition, ppm	705	790	820	790	615	660	680	660
Material Balance, (Out/In) X100								
Carbon	96.3	100.0	101.0	102.0	91.8	89.7	90.6	95.4
Oxygen	102.0	104.0	98.8	102.3	98.8	99.3	103.5	98.2
Sulfur	116.0	113.0	112.0	108.0	117.0	119.0	117.0	

APPENDIX 4

Summary of Operations - Alundum and $CaSO_4$ Beds (Con't)

Run Number	35A	35B	35C	35D	35E
Run Length, Hrs.	1	1	1	1	1
Bed Material	←	←	$CaSO_4$	→	→
Bed Material, $\bar{d}p$	←	←	1000 μ	→	→
Bed Temperature, °F	1400	1500	1600	1700	1800
Coal Feed Rate, lbs/hr	2.39	2.13	1.99	1.76	1.80
Air Rate, CFM	5.03	4.78	4.55	4.33	4.14
Percentage Stoich. Air	94.2	100.1	103.0	110.0	103.0
Carbon Loss in Fly Ash, %	19.0	14.8	13.5	12.6	10.1
Flue Gas Analysis, (dry)					
CO_2	13.2	13.0	14.0	14.2	14.4
O_2	4.7	4.5	4.4	4.0	4.0
N_2	--	--	--	--	--
CO	6000+	4650	2250	500	250
SO_2	2700	2575	2500	2475	2700
NO	300	540	610	640	680
NO Added to Fluidizing Gas, ppm	252	252	253	253	253
Flue NO After Addition, ppm	310	560	630	670	725
Material Balance, (Out/In) X100					
Carbon	96.3	92.6	97.8	103.4	96.3
Oxygen	98.3	98.3	102.3	102.3	102.2
Sulfur	116.0	114.0	107.0	119.0	117.0

APPENDIX 4

Summary of Operations - Alundum and $CaSO_4$ Beds (Con't)

Run Number	16A	16B	16C
Research Notebook	514	514	----
Bed Material	← ~20% Sulfated Lime N-1359 →		
Bed Temperature, °F	1600	1600	1600
Coal Rate, lbs/hr	1.14	1.50	1.20
Air Rate, CFM	2.27	2.27	2.27
Percentage Stoichiometric Air	88	68	83
Superficial Gas Velocity, FPS	3	3	3
Flue Gas Analysis (Dry)			
O_2, %	1.0	0	0.5
CO, ppm	←	6000+	→
NO, ppm	780	0	715

APPENDIX 5

Sample Calculation of Fractional Conversions to NO

Fuel Nitrogen

Nitrogen content of coal = 1.4 weight percent

Run 35E

NO emissions for complete conversion of fuel nitrogen to NO

Avg coal rate = 1.80 lbs/hr

combustion eff. = 90%

Air rate = 4.14 ft^3/min

$$1.80 \frac{\text{lbs coal}}{\text{hr}} \times 0.90 \times 0.014 \frac{\text{lbs N}}{\text{lbs coal}} \times \frac{\text{lb mole}}{14 \text{ lbs N}} \times \frac{379 \text{ ft}^3}{\text{lb mole}} \times \frac{\text{min}}{4.14 \text{ ft}^3} \times \frac{\text{hr}}{60 \text{ min}}$$

= 2470 ppm NO (dry)

where negligible gas expansion is assumed on a dry basis

Fractional conversion of fuel N to NO = $\frac{680}{2470} = \underline{0.275}$

where outlet NO = 680 ppm (dry)

NO added to fluidizing gas

Inlet NO concentration (based on total gas flow through the reactor) = 253 ppm

Increase in Flue Gas NO concentration = 45 ppm

Fractional conversion of added N to NO = $\frac{45}{253} = 0.178$

(Fractional retention of added NO)

APPENDIX 6

Summary of Studies of NO - SO_2 Reaction System

Run Number	3A	3B	3C	4	9A	9B	9C	9D
Research Notebook	514	514	514	514	514	514	514	514
Bed Material	Alundum	Alundum	Alundum	$CaSO_4$	$CaSO_4$	$CaSO_4$	$CaSO_4$	$CaSO_4$
Bed Weight, grams	300	300	300	300	150	150	150	150
Bed Temperature, °F	1600	1600	1600	1600	1600	1600	1500	1500
Bed Height, inches	2.3	2.3	2.3	4.7	2.3	2.3	2.3	2.3
Gas Flow Rate, CFM	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91
Superficial Gas Velocity, fps	1.42	1.42	1.42	1.42	1.42	1.42	1.35	1.35
Inlet Gas Composition								
NO, ppm	856	856	856	859	1025	992	1030	1019
SO_2, ppm	890	1895	1850	---	650	750	675	825
N_2, %	Bal.	Bal.	79.	Bal.	Bal.	79.	Bal.	79.
O_2, %	---	---	21.	---	---	21.	---	21.
Outlet Gas Composition								
NO, ppm	848	860	820	848	1015	954	1035	954
SO_2, ppm	875	1860	1850	---	650	750	675	700
NO_2, ppm	---	---	40	---	---	50	---	55
N_2, %	Bal.	Bal.	79.	Bal.	Bal.	79.	Bal.	79.
O_2, %	---	---	21.	---	---	21.	---	21.

APPENDIX 6

Summary of Studies of NO - SO_2 Reaction System

Run Number	10A	10A	10B	10B	11A	11A	11B	11B
Research Notebook	514		514		514		514	
Bed Material	Lime*		Lime*		Lime*		Lime*	
Bed Weight, grams	150		150		75		75	
Bed Temperature, °F	1500		1500		1500		1500	
Bed Height, inches	2.3		2.3		1.2		1.2	
Gas Flow Rate, CFM	0.91		0.91		0.91		0.91	
Superficial Gas Velocity, fps	1.35		1.35		1.35		1.35	
Inlet Gas Composition								
NO, ppm	585		585		1015		1015	
SO_2, ppm	670		1750		670		1975	
N_2, %	Bal.		Bal.		Bal.		Bal.	
O_2, %	---		---		---		---	
Outlet Gas Composition								
Time After Introduction of Gas to Reactor, min.	In.**	15	In.	15	In.	15	In.	15
NO, ppm	560	535	400	325	933	938	850	870
SO_2, ppm	370	390	1265	1410	340	370	1180	1460
NO_2, ppm	---	---	---	---	---	---	---	---
N_2, %	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
O_2, %	---	---	---	---	---	---	---	---

* 16.6 percent sulfated lime N-1359 removed from Esso fluid bed bed combustor at 90 percent SO_2 removal.

** Initial, approximately 2 minutes.

APPENDIX 6

Summary of Studies of NO - SO_2 Reaction System

Reactor = 2.25 In. ID Ceramic Tube (Electrically-heated)

Run Number	12A	12A	12B	12B	13A	13A	14A	14A
Research Notebook	514		514		514		514	
Bed Material	Lime*		Lime*		Lime*		Lime*	
Bed Weight, grams	75		75		300		75	
Bed Temperature, °F	1500		1500		1500		1500	
Bed Height, inches	1.2		1.2		4.7		1.2	
Gas Flow Rate, CFM	0.91		0.91		1.82		0.91	
Superficial Gas Velocity, fps	1.35		1.35		2.70		1.35	
Inlet Gas Composition								
NO, ppm	2110		2110		585		485	
SO_2, ppm	700		1900		1950		700	
N_2, %	Bal.		Bal.		Bal.		Bal.	
O_2, %	---		---		---		---	
Outlet Gas Composition								
Time after Introduction of Gas to Reactor, min.	In.	15	In.	15	In.	15	In.	15
NO, ppm	2035	1990	1885	1835	370	382	435	460
SO_2, ppm	400	400	1350	1400	1590	1710	480	460
NO_2, ppm	---	---	---	---	---	---	---	---
N_2, %	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
O_2, %	---	---	---	---	---	---	---	---

APPENDIX 6

Summary of Studies of NO - SO_2 Reaction System

Reactor = 2.25 In. ID Ceramic Tube (Electrically-heated)

Run Number	14B	14B	18A	18A	18B	18B	19A	19A
Research Notebook	514		514		514		514	
Bed Material	Lime*		Lime*		Lime*		Lime*	
Bed Weight, grams	75		75		75		75	
Bed Temperature, °F	1500		1600		1600		1500	
Bed Height, inches	1.2		1.2		1.2		1.2	
Gas Flow Rate, CFM	0.91		0.90		0.90		0.945	
Superficial Gas Velocity, fps	1.35		1.40		1.40		1.40	
Inlet Gas Composition								
NO, ppm	485		485		485		485	
SO_2, ppm	1900		700		1900		700	
N_2, %	Bal.		Bal.		Bal.		Bal.	
O_2, %	---		---		---		---	
Outlet Gas Composition								
Time after Introduction of Gas to Reactor	In.	15	In.	15	In.	15	In.	15
NO, ppm	415	363	452	458	300	275	405	455
SO_2, ppm	1210	1400	420	420	1400	1400	420	400
NO_2, ppm	---	---	---	---	---	---	---	---
N_2, %	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
O_2, %	---	---	---	---	---	---	---	---

APPENDIX 6

Summary of Studies of NO - SO_2 Reaction System

Reactor = 2.25 inch ID ceramic tube (Electrically-heated)

Run Number	19B	19B
Bed Material	Lime*	
Bed Weight, grams	75	
Bed Temperature, °F	1400	
Bed Height, inches	1.2	
Gas Flow Rate, CFM	1.0	
Superficial Gas Velocity, fps	1.40	
Inlet Gas Composition		
NO, ppm	485	
SO_2, ppm	700	
N_2, %	Bal.	
O_2, %	---	
Outlet Gas Composition		
Time after flow Started to Reactor	In.	15
NO, ppm	382	377
SO_2, ppm	400	400
NO_2, ppm	---	---
N_2, %	Bal.	Bal.
O_2, %	---	---

APPENDIX 7

Method of Sulfating Lime N-1359 For Use in Fixed Bed Reactor Studies

Lime N-1359 was used in fixed bed reactor studies to investigate the NO-SO_2-CaO reaction system. This lime was prepared in the Esso FBC by batch-charging the desired amount of lime to the combustor and continuously feeding coal. The partially-sulfated lime was removed from the combustor at the sulfation level at which it was still capable of removing 90 percent of the SO_2 from the flue gas. Details of the runs made to prepare this stone are given in the following table. Two batches of stone were prepared and used.

Run Number	6	17
Run Length, hrs.	4.0	3.9
Coal Feed Rate, lbs/hr.	0.90	0.93
Settled Bed Height, Inches	6.0	6.0
Superficial Gas Velocity, fps	3.0	3.0
Percentage Stoichiometric Air	114.	110.
Flue Gas Composition (dry)		
O_2, %	4.5	4.0
CO, ppm	350	370
Characteristics of Lime Removed from Combustor		
CaO Utilization, %	16.6	16.8
SO_2 Removal, %	90.	90.
$(\bar{dp})$, μ	930	930